Canadian
Journal of Physics

Manuscripts should be addressed to:

> DR. LÉO MARION,
> Editor-in-Chief,
> Canadian Journal of Physics,
> National Research Council,
> Ottawa, Canada.

Each manuscript should be typewritten, double-spaced, and the original and one extra copy submitted (see **Notice to Contributors,** inside of back cover).

Subscription, renewals, and orders for back numbers should be addressed to:

> Administrative Services,
> National Research Council,
> Ottawa, Canada.

Subscription rate: $3.00 a year; single numbers: 50 cents. Special rates can be obtained for subscriptions to more than one of the Journals published by the National Research Council.

LETTERS TO THE EDITOR

For the September 1952 and subsequent issues of the Canadian Journal of Physics, *Letters to the Editor*, meant to provide prompt publication of brief reports of important discoveries in physics, will be accepted. These should not exceed 600 words and, for any issue, should be submitted not later than six weeks previous to the first day of the month of issue. In order to expedite publication, galley proof will be checked in the Publications Office and will not be sent to authors. Hence, orders for reprints in excess of the 50 supplied free must accompany the manuscript.

THE INTENSITIES OF HARMONIC BANDS OF THE HD MOLECULE[1]

BY TA-YOU WU

ABSTRACT

The approximate intensity ratio 1:3 or 1:4 for the 4–0 and 3–0 vibrational bands of HD observed by Herzberg seems rather high on the basis of the usual anharmonicity considerations. To understand this, the problem is discussed qualitatively on the basis of classical mechanics. A quantum mechanical calculation of the intensities of various vibrational transitions is made by an extension of the perturbation theory treatment by Wick for the fundamental band. The relative intensities of the various vibrational bands are finally expressed as a function of the ratio $\xi = a(0;1)/a(0;0)$ of the matrix elements, with respect to the vibrational states 1 and 0, of a quantity closely resembling the polarizability of the molecule. For the 4–0 and 3–0 bands, the intensity ratio $I(4-0)/I(3-0)$ does not depend very much on the ratio ξ and has the value ~ 0.27, in agreement with the approximate observed value. The case of the molecular ion HD^+ is also briefly discussed.

It is well known that the vibrational transitions in symmetrical diatomic molecules like H_2, D_2 are inactive as dipole radiation in emission and absorption on account of the symmetry of the electric charges during the vibrational motion. In the HD molecule, however, on account of the difference in mass between the H and the D atoms, there is a relative displacement between the electric center of the two electrons and that of the two nuclei during the vibrational motion, so that vibrational transitions are accompanied by changes in the electric dipole moment of the system and become active in emission and absorption. Recently, by using a long absorption path, Herzberg has observed and measured a number of lines of the 4–0 and 3–0 vibrational bands in the photographic infrared (2). The most interesting feature of the observation seems to be the rather high value for the ratio of the intensities of the bands, namely, $I(4-0)/I(3-0) = 1:3$ or $1:4$. This ratio seems greater than the usual value for two successive harmonic bands in diatomic molecules. It is hence of interest to understand this observed intensity ratio both classically and on the basis of quantitative calculations according to quantum mechanics. The present note gives the result of such a study.

Let us first treat the problem according to classical mechanics and simplify the problem by replacing the two electrons by a single particle of charge $-2e$ and mass $2m$. Let the coordinates of this negative charge and the two nuclei, of masses M_1 and M_2, be x, x_1, x_2 respectively, all measured along the line of the nuclei. Let

$$R = x_1 - x_2, \qquad \zeta = x - \tfrac{1}{2}(x_1 + x_2),$$
$$S\eta = 2mx + M_1x_1 + M_2x_2, \qquad S = M_1 + M_2 + 2m,$$

so that R is the separation of the two nuclei, ζ the distance between the negative

charge $- 2e$ and the center of the positive charges of the nuclei, and η is the co-ordinate of the center of mass of the system as a whole. The kinetic energy of vibration of the system is

$$(1) \qquad 2T = \frac{M_1 + M_2}{S}[\mu(1 + \lambda)\dot{R}^2 + 2m\dot{\zeta}^2 + 2m\Delta\dot{R}\dot{\zeta}],$$

where

$$(2) \qquad \lambda = \frac{m}{2\mu}, \quad \mu = \frac{M_1 M_2}{M_1 + M_2}, \quad \Delta = \frac{M_1 - M_2}{M_1 + M_2}.$$

Let us assume the simple potential energy

$$2V = k\zeta^2 + K(\delta R)^2.$$

The frequencies of the two normal vibrations can be shown to be given by

$$(3) \qquad \begin{aligned} (2\pi\nu_1)^2 &\cong \frac{k}{2m}[1 + (1 + 2\Delta^2)\lambda], \\ (2\pi\nu_2)^2 &\cong \frac{K}{\mu}\left[1 + \Delta^2\lambda - \Delta^2\left(1 + \frac{4K}{k}\right)\lambda^2\right]. \end{aligned}$$

The two normal coordinates X_1, X_2 are given approximately by

$$(4) \qquad \begin{aligned} \zeta &= C[1 + (1 + 2\Delta^2)\lambda]X_1 + 2\,\frac{K}{k}\,\Delta\lambda\,D\,X_2, \\ \delta R &= -C \qquad 2\Delta\lambda \quad X_1 - (1 + \Delta^2\lambda)D\,X_2, \end{aligned}$$

where C, D are constants. In the high-frequency normal vibration X_1, the amplitude of the nuclear motion is small compared with that of the electronic motion, being $2\Delta\lambda = 4m(M_1 - M_2)/M_1 M_2$ of the latter. In the low-frequency normal vibration X_2, δR is arbitrary, but the electronic displacement ζ from the center of the positive charges is $2(K/k)\Delta\lambda = 4Km(M_1 - M_2)/M_1 M_2 k$ of δR. It is seen that had it not been for the asymmetry $M_1 - M_2 \neq 0$, ζ and δR would have been the normal coordinates themselves.

The electric moment of the system is given by

$$(5) \qquad \begin{aligned} \mathfrak{M} &= -2e[x - \tfrac{1}{2}(x_1 + x_2)] = -2e\,\zeta \\ &= -2e\left[C(1 + (1 + 2\Delta^2)\lambda)X_1 + 2\frac{K}{k}\Delta\lambda\,D\,X_2\right]. \end{aligned}$$

The term in X_1 having the high frequency $\frown (k/2m)^{\frac{1}{2}}$ may be identified with the electric moment due to the motion of the electrons relative to the nuclei as a whole. The term in X_2 having the low frequency $\frown (K/\mu)^{\frac{1}{2}}$ is the electric moment associated with the vibrational motion of the nuclei and it vanishes only if $M_1 = M_2$. This term gives rise to the emission and absorption of the vibrational band in the infrared.

If the motion is strictly simple harmonic, only the fundamental frequency will be observable as dipole radiation. If the anharmonicity of the motion is taken into account, then the electric moment $\mathfrak{M} = -2e\zeta$ will no longer be given by the

above expression in the normal coordinates but by a Fourier series of the two fundamental frequencies ν_1 and ν_2 of the form

$$(6) \qquad \mathfrak{M}(t) = -2e \sum_n [N_n \exp (2\pi i n \nu_1 t) + Q_n \exp (2\pi i n \nu_2 t)]$$

where the coefficients are determined by two effects, namely, the anharmonicity in the potential which is independent of the nuclear masses, and the term containing the difference $M_1 - M_2$ in the kinetic energy expression which acts as a perturbation on the anharmonic oscillator. On account of this effect, the intensities of the harmonic bands of the system will be different from those arising from the anharmonicity alone. The problem of intensities is much more easily treated by the method of quantum mechanics, as we shall show below.

It is of interest to consider in this connection the molecular ion HD^+. In this case, all the above calculations of the normal vibrations hold; but now the electric moment of the system is

$$(7) \qquad \mathfrak{M}(HD^+) = -e(x - x_1 - x_2) = -2e(\zeta - \tfrac{1}{2}x).$$

On expressing this in terms of the normal coordinates X_1 and X_2 and neglecting small quantities containing $\lambda = m/4\mu$ compared with unity (the electron mass being now m instead of $2m$ for HD), one obtains

$$(8) \qquad \mathfrak{M}(HD^+) = -2e[C X_1 - D \tfrac{1}{2}\Delta X_2].$$

Thus it is seen that in the normal vibration X_2, $\mathfrak{M}(HD^+)$ is about $\mu K/2mk$ or 10^3 times greater than that in the HD molecule. The intensity of the infrared absorption band of HD^+ will hence be about 10^6 times greater than that of HD. This is due to the presence of a net positive charge oscillating with the molecule in HD^+ which is not present in the case of the HD molecule. An attempt to observe the spectrum of HD^+ corresponding to the normal mode X_2 was made by Herzberg at the University of Michigan in 1939 without success, apparently because of lack of sufficient number of HD^+ ions.

To treat the problem of the relative intensities of the various vibrational transitions of HD according to the quantum mechanics, we shall follow Wick (3) who has given the treatment for the fundamental band. Since we are primarily concerned with the electric moment of the molecule along the line of nuclei, we shall introduce the coordinates z_1, z_2 for the two electrons measured from the electrical center of the two nuclei, along the line of the nuclei. Let R be the separation between the two nuclei and η the coordinate of the center of mass of the whole system. It can be easily shown that apart from terms representing the kinetic energy of the electrons due to the component motions perpendicular to the nuclear axis, the Hamiltonian of the system is, with the notation in Equation (2),

$$H = -\frac{h^2}{8\pi^2 S}\frac{\partial^2}{\partial \eta^2} + \text{potential energy due to the electrons and the nuclei}$$

$$(9) \qquad -\frac{h^2}{8\pi^2}\left[\frac{1}{4\mu}\left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\right)^2 + \frac{1}{m}\left(\frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial z_2^2}\right) + \frac{1}{\mu}\frac{\partial^2}{\partial R^2} + \frac{\Delta}{\mu}\frac{\partial}{\partial R}\left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\right)\right].$$

The first term represents the kinetic energy of the system as a whole, the terms in z_1, z_2 represent the kinetic energy of the electrons due to motions along the line of nuclei, the term in R is the energy of relative motion of the two nuclei, and the last term involving both the electronic and the nuclear coordinates represents the coupling between the vibrational and the electronic motions. This last term vanishes for the symmetrical molecule $M_1 = M_2$, and, for the case $M_1 \neq M_2$, is responsible for the activity of the vibrational transitions in absorption and emission.

For the HD$^+$ ion, there is only one electron so that the Hamiltonian (9) becomes

$$H = -\frac{h^2}{8\pi^2 S}\frac{\partial^2}{\partial\eta^2} + \text{ potential energy due to the electron and the nuclei}$$

$$(10) \qquad -\frac{h^2}{8\pi^2}\left[\left(\frac{1}{m} + \frac{1}{4\mu}\right)\frac{\partial^2}{\partial z^2} + \frac{1}{\mu}\frac{\partial^2}{\partial R^2} + \frac{\Delta}{\mu}\frac{\partial}{\partial R}\frac{\partial}{\partial z}\right].$$

It is seen that the part in square brackets here is the quantum transcription of the classical expression (1) if $2m$ in (1) is replaced by m.

For the HD molecule, the Schrödinger equation is obtained from the Hamiltonian (9). To solve this equation, we shall treat the last term in Δ as a perturbation on the system of a symmetrical molecule of reduced mass μ. We shall denote this last term by H' and write

$$(11) \qquad H' = PG, \quad P = \frac{h^2}{8\pi^2}\frac{\Delta}{\mu}\frac{\partial}{\partial R}, \quad G = \frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}.$$

The wave function of the perturbed system in the electronic state n and vibrational state v is

$$(12) \qquad \Psi_{n,v} = \Psi_{n,v}^0 + \sum_{m,u}' \frac{(m,u|H'|n,v)}{E_{n,v} - E_{m,u}}\Psi_{m,u}^0$$

where $\Psi_{n,v}^0$, $E_{n,v}$ are the wave function and energy respectively of the state n,v of the unperturbed system, and

$$(13) \qquad (m,u|H'|n,v) = \iint \Psi_{m,u}^{*0} H' \Psi_{n,v}^0 \, d\tau_{\text{el}} \, d\tau_{\text{vib}}.$$

The prime in the summation in (12) indicates that the summation is taken over all intermediate states m,u except $m = n$ and $u = v$. The matrix element (13) can be written, according to the rule of matrix multiplication,

$$(14) \qquad (m,u|H'|n,v) = \sum_{k,s}(m,u|P|k,s)(k,s|G|n,v)$$

where the matrix elements of P and G are taken with respect to the unperturbed wave functions, as in (13). The reason for writing (13) in the form (14) is that the matrix elements of P and G can be expressed in terms of the matrix elements of R and $Z(= z_1 + z_2)$ respectively.

Consider for example the Schrödinger equation for any three-dimensional motion

$$\Delta^2 \psi_v + \frac{8\pi^2\mu}{h^2}(E_v - V)\psi_v(r) = 0.$$

On multiplying this by $x\psi_s^*$, a similar equation for ψ_s^* by $x\psi_v$, subtracting one resulting equation from the other, integrating over $\mathbf{r}$ and using the boundary conditions of the ψ's, one obtains the relation

$$(15) \qquad \frac{4\pi^2\mu}{h^2}(E_s - E_v)\int \psi_s^* \, x\psi_v \, d\mathbf{r} = - \int \psi_s^* \frac{\partial}{\partial x}\psi_v \, d\mathbf{r}.$$

For our oscillator of reduced mass $\mu = M_1 M_2/(M_1 + M_2) = \frac{2}{3}M_1$, we have, from (11)

$$(16) \qquad (m, u|P|k, s) = -\tfrac{1}{6}(E_{m.u} - E_{k.s})(m, u|R|k, s).$$

Similarly one obtains the following relation

$$(17) \qquad (k, s|G|n, v) = -\frac{4\pi^2 m}{h^2}(E_{k.s} - E_{n.v})(k, s|Z|n, v)$$

where $Z = z_1 + z_2$.

The electric moment of the system HD is, from the definition of the coordinates z_1, z_2,

$$(18) \qquad \mathfrak{M} = -eZ, \qquad Z = z_1 + z_2.$$

The matrix element of the electric moment between the vibrational states v, w of the normal electronic state is, up to the first order,

$$\mathfrak{M}(0, v; 0, w) = -e(0, v|Z|0, w) - e\sum_{m.u}{}' \frac{(0, v|H'|m, u)}{E_{0.v} - E_{m.u}}(m, u|Z|0, w)$$

$$(19) \qquad\qquad - e\sum_{m.u}{}' \frac{(m, u|H'|0, w)}{E_{0.w} - E_{m.u}}(0, v)|Z|m, u).$$

The matrix element $(0, v|Z|0, w)$ for the unperturbed system is obviously zero since the electronic part of the unperturbed Ψ^0 is symmetric with respect to the midpoint of the internuclear line. Hence, on substituting (16) and (17) into (19), and noting that

$$E_{m.u} - E_{k.s} = E_{m.u} - E_{0.w} + E_{0.w} - E_{k.s},$$

$$E_{k.s} - E_{m.u} = E_{k.s} - E_{0.v} + E_{0.v} - E_{m.u},$$

we obtain, again on using the matrix product rule similar to (14),

$$\mathfrak{M}(0, v; 0, w) = \frac{4\pi^2 me}{h^2} {\sum_{m,u}}' \left[- (0, v|PZ|m, u)(m, u|Z|0, w) \right.$$

$$\left. + (0, v|Z|m, u)(m, u|ZP|0, w) \right]$$

$$+ \frac{4\pi^2 me}{h^2} {\sum_{m,u}}' \sum_{k,s} \left\{ \nu_{0v;ks} \frac{(0, v|P|k, s)(k, s|Z|m, u)(m, u|Z|0, w)}{E_{0,v} - E_{m,u}} \right.$$

$$\left. - \nu_{0w;ks} \frac{(0, v|Z|m, u)(m, u|Z|k, s)(k, s|P|0, w)}{E_{0,w} - E_{m,u}} \right\}.$$

The prime in the first sum indicates the exclusion of the state $m,u = 0,v$; that in the second sum, of the state $m,u = 0,w$. On first including these terms in the respective sums and then subtracting them again, the first two sums reduce to

$$\frac{4\pi^2 me}{h^2} \left[- (0, v|PZ^2|0, w) + (0, v|Z^2 P|0, w) \right]$$

$$+ \frac{4\pi^2 me}{h^2} \left[(0, v|PZ|0, v) - (0, w|ZP|0, w) \right](0, v|Z|0, w) = 0$$

since $(0, v|Z|0, w) = 0$ as noted before and $PZ^2 = Z^2 P$. Hence we have

$$\mathfrak{M}(0, v; 0, w) = \frac{4\pi^2 me}{h} \sum_{k,s} \left\{ \nu_{0v;ks}(0, v|P|k, s) {\sum_{m,u}}' \frac{(k, s|Z|m, u)(m, u|Z|0, w)}{E_{0,v} - E_{m,u}} \right.$$

$$\left. - \nu_{0w;ks}(k, s|P|0, w) {\sum_{m,u}}' \frac{(0, v|Z|m, u)(m, u|Z|k, s)}{E_{0,w} - E_{m,u}} \right\}.$$

Since in these sums m is to be different from 0, i.e., the summations are to be taken over all excited electronic states, and since the energy difference between different electronic states is in general large compared with that between vibrational states, we can approximate $E_{0,v} - E_{m,u}$ in the first denominator by $E_{0,w} - E_{m,u}$, and the $E_{0,w} - E_{m,u}$ in the second denominator by $E_{0,v} - E_{m,u}$. Since P does not contain the electronic coordinates and since the electronic wave functions of different electronic states for any fixed R are orthogonal, the matrix elements $(0, v|P|k, s)$, $(k, s|P|0, w)$ will vanish unless k is also the normal electronic state 0. Hence we obtain finally

$$\mathfrak{M}(0, v; 0, w) = \frac{4\pi^2 m}{he} \sum_s \left\{ \nu_{v;s}(0, v|P|0, s)(0, s|\mathbf{a}|0, w) \right.$$

(20)
$$\left. - \nu_{w;s}(0, v|\mathbf{a}|0, s)(0, s|P|0, w) \right\}$$

where we have introduced the quantity $\mathbf{a}$ whose matrix elements are given by

(21)
$$(0, s|\mathbf{a}|0, w) = e^2 {\sum_{m,u}}' \frac{(0, s|Z|m, u)(m, u|Z|0, w)}{E_{0,w} - E_{m,u}},$$

$$(0, v|\mathbf{a}|0, s) = e^2 {\sum_{m,u}}' \frac{(0, v|Z|m, u)(m, u|Z|0, s)}{E_{0,v} - E_{m,u}},$$

and

$$h\nu_{v;s} \equiv h\nu_{0v;ks} = E_{0,v} - E_{0,s}.$$

Equation (20) can be put, on using (16), in the following form

(22)
$$\mathfrak{M}(0, v; 0, w) = \frac{2\pi^2 m}{3e} \sum_s \left\{ \nu_{v;s}^2 (0, v|R|0, s)(0, s|a|0, w) \right.$$
$$\left. + \nu_{w;s}^2 (0, v|a|0, s)(0, s|R|0, w) \right\}.$$

The quantity a given by (21) is seen to be closely related to the polarizability of the molecule.

We shall now apply (20) or (22) to the fundamental and harmonic bands of the HD molecule. We see that if we assume the vibrational motion to be harmonic, all matrix elements $(0, v|R|0, s)$, $(0, w|R|0, s)$ vanish except for $v = s + 1$ and $w = s + 1$ respectively. In this case, only the fundamental will be observed. In order to account for the appearance of the harmonics, it is necessary to work with an anharmonic oscillator, say, of the Morse type, as our initial approximation to (9). We shall now use the simplified notation

$$\mathfrak{M}(v; w) = \mathfrak{M}(0, v; 0, w),$$

$$R(v; w) = (0, v|R|0, w),$$

$$a(v; w) = (0, v|a|0, w),$$

(23)
$$K = \frac{2\pi^2 m}{3e}.$$

Then

$$\mathfrak{M}(0; 1) = K[\nu_{01}^2 a(1; 1)R(0; 1) + \nu_{10}^2 a(0; 0)R(1; 0) + \nu_{02}^2 a(1; 2)R(0; 2)$$
$$+ \nu_{12}^2 a(0; 2)R(2; 1) \ldots],$$

$$\mathfrak{M}(0; 2) = K[\nu_{02}^2 a(2; 2)R(0; 2) + \nu_{20}^2 a(0; 0)R(2; 0) + \nu_{01}^2 a(2; 1)R(0; 1)$$
$$+ \nu_{21}^2 a(0; 1)R(2; 1) + \nu_{03}^2 a(2; 3)R(0; 3) + \nu_{23}^2 a(0; 3)R(2; 3) \ldots],$$

$$\mathfrak{M}(0; 3) = K[\nu_{03}^2 a(0; 0)R(0; 3) + \nu_{30}^2 a(3; 3)R(3; 0) + \nu_{13}^2 a(3; 1)R(1; 0)$$
(24)
$$+ \nu_{02}^2 a(3; 2)R(2; 0) + \nu_{23}^2 a(0; 2)R(2; 3) + \nu_{01}^2 a(3; 1)R(1; 0)$$
$$+ \nu_{43}^2 a(0; 4)R(4; 3) + \nu_{04}^2 a(3; 4)R(4; 0) + \ldots],$$

$$\mathfrak{M}(0; 4) = K[\nu_{04}^2 a(0; 0)R(0; 4) + \nu_{40}^2 a(4; 4)R(4; 0) + \nu_{41}^2 a(0; 1)R(1; 4)$$
$$+ \nu_{03}^2 a(4; 3)R(3; 0) + \nu_{42}^2 a(0; 2)R(2; 4) + \nu_{02}^2 a(4; 2)R(2; 0)$$
$$+ \nu_{43}^2 a(0; 3)R(3; 4) + \nu_{01}^2 a(4; 1)R(1; 0) + \nu_{45}^2 a(0; 5)R(5; 4)$$
$$+ \nu_{05}^2 a(4; 5)R(5; 0) + \ldots].$$

Now for the Morse oscillator, the matrix elements $R(v;w)$ as they stand cannot be evaluated easily. One can use, however, the relation (16), and for an oscillator of reduced mass $\mu = \frac{2}{3}M_1$, we have

$$R(v;w) = \int_0^\infty \psi_v R\psi_w \, dR = \frac{3h}{8\pi^2 M_1 \nu_{v;w}} \int_0^\infty \psi_v \frac{d\psi_w}{dR} \, dR,$$

where

$$\int_0^\infty \psi_v \frac{d\psi_w}{dR} \, dR = -\int_0^\infty \psi_w \frac{d\psi_v}{dR} \, dR.$$

For a Morse oscillator, these integrals can be analytically evaluated in a closed form, namely,*

$$(25) \quad \int_0^\infty \psi_v \frac{d\psi_w}{dR} \, dR =$$

$$\frac{1}{2}\left[\frac{8\pi^2\mu}{h}\right]^{\frac{1}{2}} \left[\frac{v![1 - (2w + 1)x_e][1 - (2v + 1)x_e]v}{w![1 - (w + 1)x_e][1 - (w + 2)x_e]\ldots[1 - vx_e]} x_e^{v-w-1}\right]^{\frac{1}{2}}$$

where $v > w$, and

$$(26) \qquad\qquad x_e = \frac{\omega}{4D} = 0.026 \text{ for HD},$$

ω, D being the vibrational frequency and dissociation energy respectively, both in cm.$^{-1}$ Hence we obtain

$$(27) \quad R(v;w) = \frac{A}{[1 - (v + w + 1)x_e].(v - w)}$$

$$\times \left[\frac{v![1 - (2w + 1)x_e][1 - (2v + 1)x_e]}{w![1 - (w + 1)x_e]\ldots[1 - vx_e]}\right]^{\frac{1}{2}} x_e^{\frac{1}{2}(v-w-1)},$$

$R(v;w)$ being equal to $R(w;v)$ of course, and

$$(28) \qquad\qquad A = \left[\frac{h}{8\pi^2\mu\nu}\right]^{\frac{1}{2}} = \left[\frac{3h}{16\pi^2 M_1\nu}\right]^{\frac{1}{2}}.$$

On putting in the empirical value for x_e in (27), one obtains

$$R(0;1) = 0.96A, \qquad R(1;2) = 1.30A, \qquad R(2;3) = 1.52A,$$

$$R(3;4) = 1.67A, \qquad R(4;5) = 1.773A, \qquad R(0;2) = 0.109A,$$

$$(29) \quad R(1;3) = 0.181A, \qquad R(2;4) = 0.244A, \qquad R(0;3) = 0.0205A,$$

$$R(1;4) = 0.040A, \qquad R(0;4) = 0.0051A, \qquad R(0;5) = 0.0015A.$$

* Integrals of the type (25) are given in Wu, T. Y. Vibrational spectra and structure of polyatomic molecules. Edward Bros., Ann Arbor, Mich. 1946. pp. 73-74. The general formula (25) is given by Rosenthal, Jenny E. Proc. Natl. Acad. Sci. N.Y. 21: 281. 1935; and Infeld, L. and Hull, T. E. Revs. Modern Phys. 23: 21. 1951.

For the matrix elements $a(v; w)$, we do not have any theoretical knowledge except that, to a good approximation, the polarizability of the molecule is about the same for different vibrational states of the same electronic state, i.e.,

$$(30) \qquad a(0; 0) \cong a(1; 1) \cong a(2; 2) \ldots.$$

Furthermore, it is very plausible to assume that the matrix elements $a(0; 1)$, $a(1; 2)$, $a(2; 3)$, etc. come from the term proportional to the normal coordinate in the expansion of a, and hence

$$(31) \qquad a(0; 1)/a(1; 2) = R(0; 1)/R(1; 2), \text{ etc.}$$

Also, from the empirical fact that the intensity of the Rayleigh scattering is very much greater than that of the Raman scattering, we shall take

$$(32) \qquad a(0; 0) \gg a(0; 1) \gg a(0; 2) \gg a(0; 3), \text{ etc.}$$

On the basis of (30), (31), (32), and with the values in (29), we obtain for the matrix elements of the electric moment for the fundamental and the harmonics the following expressions

$$\mathfrak{M}(0; 1) = 0.96 \, a(0; 0)B[1 + 0.308 \, \xi + \ldots],$$

$$\mathfrak{M}(0; 2) = 2^2 \times 0.109 \, a(0; 0)B[1 + 3.32 \, \xi + \ldots],$$

(33)

$$\mathfrak{M}(0; 3) = 3^3 \times 0.0205 \, a(0; 0)B[1 + 4.22 \, \xi + \ldots],$$

$$\mathfrak{M}(0; 4) = 4^2 \times 0.0051 \, a(0; 0)B[1 + 4.60 \, \xi + \ldots].$$

where

$$B = 2KA\nu^2 = \frac{\pi h m \nu}{e} \left[\frac{\nu}{3M_1} \right]^{\frac{1}{2}}$$

and

$$\xi = a(0; 1)/a(0; 0).$$

By means of (29), one can calculate the ratios of the intensities of the various transitions which are given by

$$I(w-0) = \frac{8\pi^2}{3h^2} h\nu_{w;0} |\mathfrak{M}(w; 0)|^2$$

in terms of the ratio ξ as a parameter. The result is shown in Fig. 1. From Fig. 1, it is seen that the ratio of the intensities of the third and the second harmonic $I(4-0)/I(3-0)$ does not depend very much on ξ, and is about 0.27, in agreement with the approximate value observed.

For the other harmonics, the intensity ratios depend on ξ. As the matrix elements of a are not known, we may perhaps make an estimate of the ratio ξ from the observed intensities of the Raman and the Rayleigh scattering, which may be taken as approximately proportional to the square of ξ. Reference to Bhaga-vantam's summary of these scattering data seems to indicate a value in the
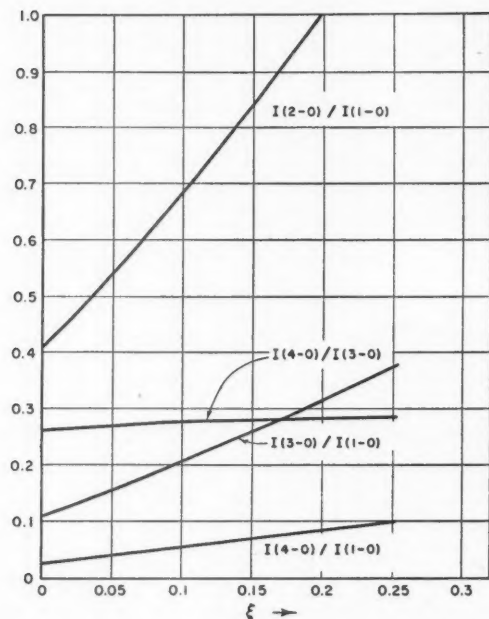
FIG. 1. Ratio of intensities of vibrational bands of HD as a function of the ratio $\xi = a(1,0)/a(0,0)$ of the molecule.

neighborhood of 0.065 for ξ for H_2 (1). This would predict an intensity ratio of about 0.55 for the first harmonic and the fundamental.

It is of interest to note that while a close examination of (22), (29), and (33) shows that the matrix elements of the electric moment and hence the relative intensities of the various transitions depend very much on the anharmonicity of the motion, the dependence of $\mathfrak{M}(0;w)$ on the quantum number w is quite different from that obtained on the consideration of a pure anharmonicity effect alone. Thus consider the limiting case of $\xi \to 0$ for simplicity. Equations (22) or (24) show that, as the result of the factor in $\nu^2_{v;s}$, the ratio of the square of the matrix elements of $\mathfrak{M}$ for the various transitions is given by

$$|\mathfrak{M}(0;1)|^2 : |\mathfrak{M}(0;2)|^2 : |\mathfrak{M}(0;3)|^2 : |\mathfrak{M}(0;4)|^2 =$$

(29) $$|R(0;1)|^2 : 16\,|R(0;2)|^2 : 81\,|R(0;3)|^2 : 256\,|R(0;4)|^2.$$

On the other hand, if one assumes that the $\mathfrak{M}(0;w)$ of the harmonics are simply given by the anharmonicity of the motion, then the ratio for the $|\mathfrak{M}(0;w)|^2$ above would have been given simply by the squares of the $R(0;w)$. It is seen that the theory predicts a much larger intensity, by a factor w^4, for the harmonic band w-0 relative to the fundamental than that indicated by the simple effect of an-

harmonicity. For the first harmonic relative to the fundamental, this factor is 16, while for the 4–0 band relative to the fundamental, it is $4^4 = 256$. This factor is further enhanced by the term depending on ξ in (33), as shown in Fig. 1. The case of the observed intensities of the 4–0 and 3–0 bands is in fact not particularly suitable for the verification or demonstration of the theory because this extra factor arising from $\nu^2_{v;s}$ is only about 3 and because intensity measurements on different infrared photographic plates are difficult. The case of the fundamental and the first harmonic, however, is much more suitable for these reasons. It is also suggested that an accurate measurement of the relative intensities of the fundamental and the first harmonic will be very interesting as a means for the determination of the ratio $a(0; 1)/a(0; 0)$.

In the case of the molecular ion HD$^+$, the electric moment of the system is

$$\mathfrak{M}(\text{HD}^+) = e(x_1 + x_2 - x)$$

(18A)
$$= e\left[\eta + \frac{M_1 - M_2}{2S}R - \left(1 + \frac{m}{S}\right)z\right].$$

Now the matrix elements of R between different vibrational states of the normal electronic state do not vanish even for the unperturbed anharmonic oscillator in (10), although on account of the factor $M_1 - M_2$ in (18A), the matrix elements of the electric moment still vanish when $M_1 = M_2$. The contribution to the matrix element of $\mathfrak{M}$ from the term in z is zero for the symmetrical oscillator and for the unsymmetrical HD$^+$ it is given by an expression similar to (22). For the part in R, one obtains, with A given by (26),

$$\mathfrak{M}_R(0; 1) = 0.96Ae,$$

$$\mathfrak{M}_R(0; 2) = 0.109Ae,$$

(33A)
$$\mathfrak{M}_R(0; 3) = 0.0205Ae,$$

$$\mathfrak{M}_R(0; 4) = 0.0051Ae.$$

Comparison with (33) shows that $\mathfrak{M}_R(0; 1)$ for HD$^+$ is greater than $\mathfrak{M}(0; 1)$ for HD by a factor $3e/(4\pi^2mv^2a) \simeq 10^3$, in agreement with the classical consideration discussed under Equation (8). Hence one can neglect the contribution from the term in z to $\mathfrak{M}$. As a result, in distinction from the case of HD, the intensities of the harmonic bands of HD$^+$ decrease more rapidly with the order of the harmonic.

The writer is grateful to Dr. G. Herzberg for calling his attention to this problem and for helpful discussions.

REFERENCES

1. BHAGAVANTAM, S. Scattering of light and the Raman effect. Chemical Publishing Company, Inc., Brooklyn, N.Y. 1942. p. 191. [Note that the a' and the a in Table 38 are in different units.]
2. HERZBERG, G. Nature, 166: 563. 1950.
3. WICK, G. C. Atti reale accad. nazl. Lincei, 21: 708. 1935.

THE NEAR ULTRAVIOLET BANDS OF N_2^+ AND THE DISSOCIATION ENERGIES OF THE N_2^+ AND N_2 MOLECULES[1]

By A. E. Douglas

ABSTRACT

The ultraviolet emission bands of N_2^+ have been photographed using a six meter grating, and a number of new bands of high vibrational quantum number have been found. It has been possible to show that the $B^2\Sigma_u^+$ state dissociates at a limit 70,358 cm.$^{-1}$ above the ground state. It is shown that these results give strong support to the value 9.75 electron volts for the dissociation energy of nitrogen, but the lower value of 7.37 electron volts cannot be eliminated with certainty. The peculiar manner in which the $B^2\Sigma$ state converges to its dissociation limit is interpreted as being caused by an interaction between the $B^2\Sigma_u^+$ and the $C^2\Sigma_u^+$ states.

A. INTRODUCTION

The dissociation energy of the ionized nitrogen molecule can be related to that of the neutral molecule through the well established ionization potentials of the nitrogen atom and molecule. It is known that the dissociation energy of nitrogen is either 78,717 cm.$^{-1}$ or 59,490 cm.$^{-1}$ (6). Each of these values has recently received support (7, 9). The corresponding values for N_2^+ are 70,358 cm.$^{-1}$ and 51,131 cm.$^{-1}$ The present investigation of the ultraviolet bands of N_2^+ was undertaken in the hope of determining which of these values is the correct one. It has not been possible to decide with certainty between the two values, but it has been demonstrated that the higher value of the dissociation energy allows a simpler interpretation of the observed spectrum.

The energy level diagram of the N_2^+ molecule is shown in Fig. 1. Transitions from the $B^2\Sigma_u^+$ state of the $X^2\Sigma_g^+$ state give rise to the well known near ultra-violet bands of N_2^+ which have been studied by a number of investigators. Herzberg (8) has given the most complete vibrational analysis of the system, while Childs (2), Coster and Brons (3), Crawford and Tsai (4), and Parker (11) have each analyzed the rotational fine structure of a number of bands. It has been realized by many investigators that the vibrational levels of the $B^2\Sigma_u^+$ state converge quite rapidly and that a short extension of the band system should allow one to determine a dissociation limit. The fact that the convergence of the levels is far from linear has made it impossible to extrapolate them far beyond the observed levels. We therefore have reinvestigated the band system in order to extend our knowledge of the vibrational levels of the B state to higher vibrational quantum numbers.

B. EXPERIMENTAL

The near ultraviolet bands of N_2^+ fall in the same spectral region as the very strong second positive bands of nitrogen. The chief experimental problem is, therefore, one of obtaining a source of the N_2^+ bands which is relatively free
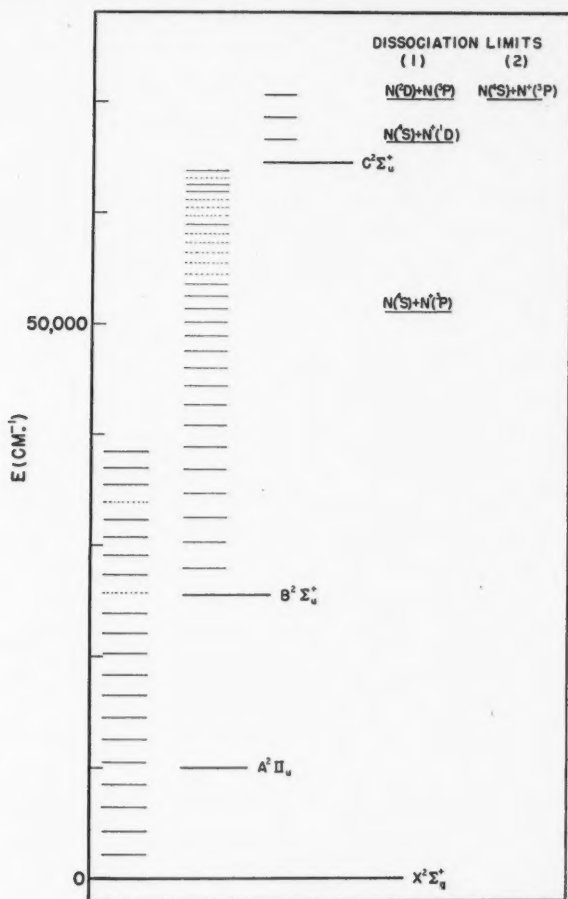
FIG. 1. Energy level diagram of the N_2^+ molecule.

The heavy horizontal lines indicate the positions of the electronic states. The short lines indicate the positions of the observed vibrational levels, and the dotted lines indicate the positions of vibrational levels that have not been observed. The position of the $A^2\Pi_u$ state is not definitely known. Vibrational levels of the $C^2\Sigma_u^+$ state above those shown here have been observed.

from bands of N_2. We have found that a discharge through helium, containing a trace of nitrogen, in a hollow cathode discharge tube gives favorable results. Though this source is not as intense as others that might have been used, the fact that it gave the bands of the second positive system only very weakly has been an important factor in allowing us to find bands which are usually overlapped by the much stronger bands of N_2.

The bands were photographed in the second and third order of a 21 ft. concave grating spectrograph. The grating, which has 15,000 lines per inch and a ruled surface of 7 in. × 3 in., was ruled by the Bausch and Lomb Company. The excellent light gathering power of this grating due to its large size and efficient blazing was a major factor in making this work possible.

C. ANALYSIS OF THE BANDS

Fourteen bands not previously recorded have been found and their rotational fine structures analyzed. Most of the new bands with $v' = 14$ or less are readily recognized on the plates since they have well developed heads. Bands resulting from the higher vibrational levels of the B state are similar to the 29–20 band

TABLE I
WAVE NUMBERS OF THE LINES OF THE VIOLET N_2^+ BANDS

K	11–8 $\nu_0 = 30998.7$ R(K)	11–8 P(K)	12–11 $\nu_0 = 26754.2$ R(K)	12–11 P(K)	13–12 $\nu_0 = 26229.4$ R(K)	13–12 P(K)	14–10 $\nu_0 = 31063.6$ R(K)	14–10 P(K)	14–11 $\nu_0 = 29226.8$ R(K)	14–11 P(K)
0	31001.96*								29232.33	
1	05.06	30995.19	26760.28*			26226.07	31071.09*	31056.14	34.49	29219.45
2	07.91	91.42	62.97	26747.06	26237.66	22.47	72.70*	51.81	36.27	15.43
3	10.51*	87.81*	65.53	43.19	40.07	18.62	73.86*	47.00	37.55	10.65
4	12.96*	83.21	67.76	39.15	42.15	14.42	74.56*	41.70		05.59
5	15.02	78.74*	69.82	34.91	44.00	10.08 09.90				
6	16.92	74.05	71.73	30.40	45.10 45.51	05.37 05.12	74.79	35.99	38.92	00.07
7	18.51 18.72	69.14	73.33 73.59	25.79 25.57		00.33 00.05	74.56*	29.78	38.92	194.21
8	19.94 20.17	64.06 63.92	74.72 75.08	20.88 20.59		195.08 94.70	73.86*	23.14	38.60	87.84
9		58.69 58.50	75.90 76.29	15.75 15.45		89.49 89.05	72.70*	16.00*	37.82	81.11
10	22.04 22.36	53.08 52.89	76.82 77.22	10.38 10.04		83.58 83.07	71.09*	08.44*	36.62	73.94
11		47.27 47.03	77.53 78.01	04.83 04.42			68.95	00.32	34.93	66.40
12		41.18 40.90	78.01 78.48	698.98 98.56			66.34	0991.80	32.85	58.34
13		34.82 34.48		92.94 92.48			63.26	82.82		49.89
14		28.24 27.90		86.63 86.13			59.71	73.34	27.50	41.00
15		21.46 21.09		80.17 79.57			55.63	63.42		31.70
16		14.40 13.97		73.40 72.73			51.23 51.06		20.16	
17		07.05 06.66		66.50 65.67			46.29 46.03	42.09	16.02	
18	20.99 20.38	899.51 99.04		59.10 58.33			40.79 40.53	30.86 30.64	11.14	
19	19.61 19.01	91.69 91.15		51.46 50.69			34.75 34.49	18.97 18.71	06.21	
20	17.97 17.26	83.62 83.03		43.23 42.67			28.30 28.01	06.41		
21	16.00* 15.36	75.23 74.63						893.88 93.51		
22	13.85* 12.96*	66.66 65.94					13.85* 13.45	80.51 80.18		
23	11.32 10.51*	57.69 56.98					05.78 05.43*			
24	08.44* 07.65	48.53 47.75					0997.28 96.94*	52.42 52.02		
25	05.43 04.42	39.06 38.18					88.24* 87.81*			
26	01.96 00.86	29.31 28.35					78.74* 78.20*			
27	30998.13 96.94*	19.23* 18.19								
28	93.83 92.59	08.80* 07.75								

Lines marked * are uncertain because of overlapping or weakness.

TABLE I (Concluded)

K	14-12 $\nu_0 = 27425.7$ R(K)	P(K)	14-16 $\nu_0 = 20587.4$ R(K)	P(K)	15-13 $\nu_0 = 26787.5$ R(K)	P(K)	16-13 $\nu_0 = 27854.6$ R(K)	P(K)	22-17 $\nu_0 = 26607.0$ R(K)	P(K)
0									26609.34	
1									11.17*	
2			20595.67	20580.81					11.85*	26599.94
3			98.06	77.15		26776.35			11.85*	95.24
4		27409.95	600.33			71.90	27863.86*	27838.64	11.17*	89.81
5		05.11	02.38	69.46		66.99	63.86*	33.20	09.72	83.60
6		399.87	04.12			61.51	63.86*	27.39	07.47	76.60
7		94.22	05.74			55.66	63.12	21.00*	04.43	68.88
8		88.28	07.16			49.37	61.84	14.13	00.70	60.38
9		81.91	08.41	51.69		42.63		06.88	596.17	51.20
10		75.17	09.36	46.71		35.56	57.75	798.84	90.85	41.09
11		68.05	10.14	41.52		27.99		90.56	84.87	30.44}
								90.36	84.68	30.21}
12		60.56	10.71	36.19		20.13}	51.79}	81.59}	77.99}	18.86}
						19.96}	51.51}	81.37}	77.74}	18.68}
13			11.12	30.53		11.61	47.79	72.12}	70.16*	06.53}
								71.90}		06.32}
14		44.74		24.82	26786.62}	02.88}		62.21}	61.93}	493.44}
					86.36}	02.66}		61.92}	61.68}	93.19}
15		35.78			83.04*}	693.59}		51.74}	52.69}	79.57}
					82.61*}	93.33}		51.44}	52.44}	79.29}
16		26.70		12.66		83.89}	33.20}	40.73}	42.71}	
						83.57}	32.77}	40.43}	42.42}	
17				06.16				29.26}		
								28.89}		
18		07.82}		499.54			21.00*}	17.20}	20.25}	
		07.30}					20.64}	16.87}	20.04}	
19									08.35*}	
									07.66*}	
20									495.02}	
									94.41}	
21									81.00}	
									80.31}	

K	26-19 $\nu_0 = 26419.7$ R(K)	P(K)	27-19 $\nu_0 = 27081.5$ R(K)	P(K)	27-20 $\nu_0 = 25583.8$ R(K)	P(K)	29-20 $\nu_0 = 26827.7$ R(K)	P(K)	29-21 $\nu_0 = 25369.5$ R(K)	P(K)
0	26422.18						26829.71		25371.74	
1	23.15*						30.50		72.74	25366.77
2	23.76	26413.03	27084.53	27073.95			30.50	26820.76	72.74	62.77
3	23.15*	08.28	83.40				29.34	15.56	71.74	57.77
4	21.57	02.45	81.86	63.31			27.13	09.55	69.74	52.07
5	19.15	395.78	79.05	56.34			23.93	02.42	66.77	45.16
6	15.78	88.19	75.26	48.35			19.59	794.21	62.77	37.29
7	11.44	79.58	70.49	39.49			14.27		57.77	28.43
8	06.23	70.16	64.77	29.58		25533.31	07.91		51.75	18.58
9	00.02	59.89	58.01	18.82		22.83	00.45		44.75	07.73
10	393.03	48.49	50.30	06.95		11.52			36.84	295.87
11	85.04	36.49*	41.37*	6994.18		499.25			27.82	83.08
12	76.09	23.10	31.87		25537.82}	86.04			17.89	69.24
					37.60}					
13	66.26	09.03	21.20	65.60	27.53	71.92			06.92	54.50
14	55.45	293.92	09.65}	49.88	16.70}	56.95			294.85	38.55
			09.51}		16.49}					
15	43.66	78.11	6997.05}	33.23}	04.64	42.43*			82.03	21.75
			96.80}	33.08}						
16	31.16}	61.31		15.54}	491.76	24.00			68.03	03.92
	30.92}			15.32}						
17			68.76}	896.85}	77.98	05.99			53.03	
			68.48}	96.64}						
18	03.01}		53.12}	77.20}	63.33}	387.43}			37.10	165.32
	02.75}		52.83}	76.94}	63.08}	87.19}				
19			36.47}	56.51}	47.52					
			36.15}	56.25}						
20	271.15}		18.81}	34.84}	31.03}				02.12}	
	70.82}		18.53}	34.57}	30.79}				01.87}	
21			00.17}	12.21}	13.35}					
			899.88}	11.92}	13.10}					
22			80.54}		394.83}	02.89}			163.02}	
			80.23}		94.54}	02.55}			62.72}	
23			59.81}		74.99					
			59.49}							
24			38.17}		54.74}					
			37.81}		54.45}					
25			15.56}							
			15.11}							

shown in Fig. 2. For these bands the head is weak since the head and the origin
are close together. In addition, bands with high v values are overlapped by
the strong sequences arising from the low vibrational levels. It therefore
appears probable that there are additional bands of high quantum number on
our plates which have not yet been recognized. The bands which have already
been found are, however, sufficient to determine within a few cm.$^{-1}$ the
positions of all the vibrational levels in both the upper and lower states up to
the highest level observed. The wave numbers of the band origins and of the
lines of the bands are given in Table I. The doublet splitting of the lines in
these bands is a highly variable quantity since it is caused by an interaction
between the B and A states. In most cases it is not possible to determine the
correct J numbering of the lines of the doublets and no attempt has been
made to do so in Table I. In the determination of the B values the average wave
numbers of the doublets were used.

The analysis of the bands presents no difficulties. The numbering of the
lines can be determined by inspection and the B values determined in the
usual way from the $\Delta_2 F(K)$ values. The vibrational numbering of the bands
likewise presented no great difficulty. If one extrapolates the curve of B_v
plotted against v to higher vibrational levels one can obtain sufficiently accurate
values of B_v to determine the vibrational numbering of new bands for which
the B values have been determined. Also one may extrapolate the curves of
$\Delta G_{v+\frac{1}{2}}$ plotted against v and predict the positions of new bands, and thereby
obtain the vibrational numbering of observed bands. These two methods of
determining vibrational numbering were sufficient to give the numbering
uniquely even over the gap of five missing vibrational levels between $v' = 16$
and $v' = 22$.

A Deslandres table of band origins used in this work is given as Table II.
From these band origins it has been found that the vibrational levels of the
lower state can be represented by

$$G''(v) = 2191.00\,v - 16.190\,v^2 - 0.0303\,v^3 - 0.00092\,v^4.$$

Though the position of a considerable number of the vibrational levels of the
ground state cannot be determined directly, there appear to be no sudden
discontinuities in their spacings and the above equation can safely be used
to determine the positions of missing levels. The vibrational levels of the upper
state cannot be represented by any simple equation. The values of $\Delta G_{v+\frac{1}{2}}$ for
the $B^2\Sigma_u^+$ state are given in Table II. In this table the values of $\Delta G_{v+\frac{1}{2}}$ that
cannot be measured directly are supplied by values that make the curve of
$\Delta G_{v+\frac{1}{2}}$ plotted against v give a smooth curve.

The values of B_v for the ground state up to $v = 14$ can be represented by
the equation

$$B_v'' = 1.932 - 0.020(v + \tfrac{1}{2}).$$

Above $v = 14$ the observed values are somewhat lower than those calculated
from the equation. The measured values of B_v'' are given in Table III. The
B values of the upper state follow no such simple equation, but those that have
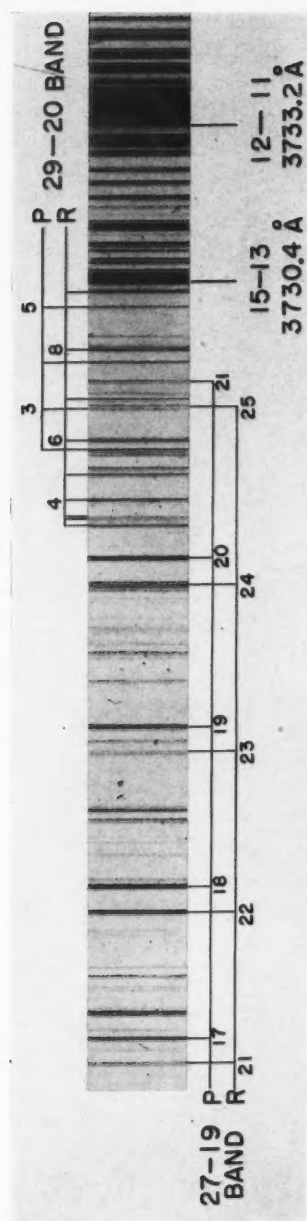been measured are given in Table III.

PLATE I

Fig. 2. A part of the spectrum of N_2^+.
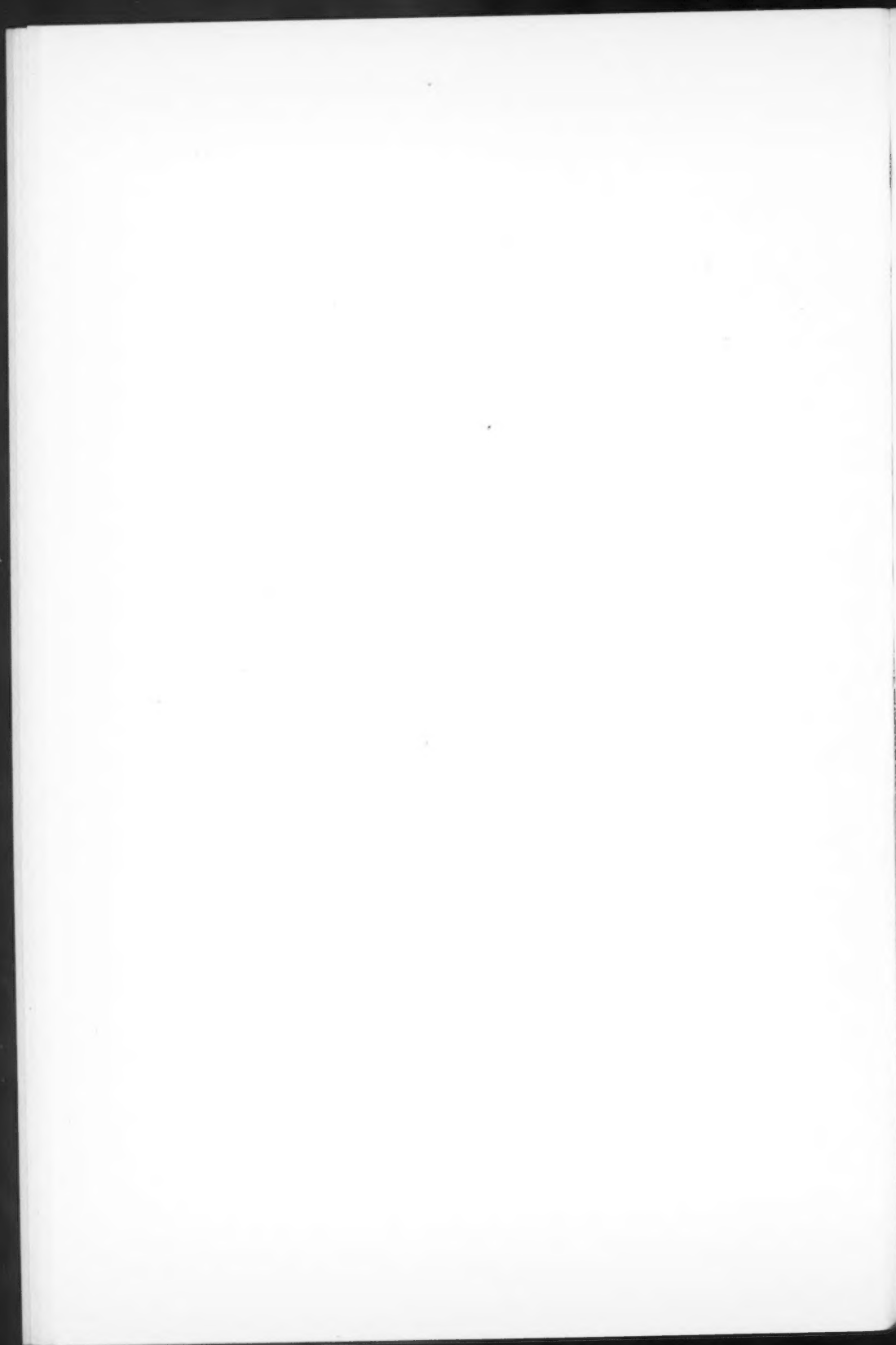The figure shows the heads of the (12–11), (15–13), and (29–20) bands of N_2^+ and a section of the (27–19) band.

TABLE II

WAVE NUMBERS OF THE BAND ORIGINS OF THE VIOLET N_2^+ BANDS

Columns = v'', rows = v'.

v' ＼ v''	0	1	2	3	4	5	6	7	8	9	10
0	25566.0[2]	23391.2[2]	21249.0[2]	19139.7[1]							
1			23620.5[2]	21511.3[2]	19434.7[1]						
2			25939.8[1]	23830.0[1]	21753.7[2]	19710.4[1]					
3					24013.9[1]	21971.1[1]					
4							22158.3[3]	20182.6[3]			
5								22305.4[1]	20365.5[3]		
6									22406.5[1]	20499.0[3]	
7											20578.0[3]
8							30112.0[2]				
9											
10									29518.8[2]	27611.8[2]	
11									30998.7[4]		
12											
13											
14											31063.6[4]

v' ＼ v''	11	12	13	14	15	16	17	18	19	20	21
12	26754.2[4]	26229.4[4]									
13	29226.8[4]	27425.7[4]	26787.5[4]								
14			27854.6[4]	21044.5[3]							
15											
16						20587.4[4]					
17											
18											
19											
20											
21							26607.0[4]				
22									26419.7[4]		
23									27081.5[4]		
24											
25											
26										25583.8[4]	
27										26827.7[4]	
28											
29											25369.5[4]

[1] Crawford and Tsai, Ref. (4).
[2] Coster and Brons, Ref. (3).
[3] Parker, Ref. (11).
[4] Present work.

TABLE III

ROTATIONAL CONSTANTS AND VIBRATIONAL QUANTA DETERMINED
FROM THE VIOLET N_2^+ BANDS

v	$X^2\Sigma_g^+$ state		$B^2\Sigma_u^+$ state	
	B	$\Delta G_{v+\frac{1}{2}}$	B	$\Delta G_{v+\frac{1}{2}}$
0	1.922	2174.8	2.073	2371.5
1	1.902	2142.2	2.049	2318.8
2	1.879	2109.4	2.025	2260.4
3	1.861	2076.4	2.002	2196.4
4	1.841	2043.0	1.968	2122.8
5	1.826	2009.2	1.926	2041.0
6	1.808	1975.7	1.896	1951.1
7	1.781	1939.9	1.852	1838.2
8	1.766	1907.0	1.810	1726.9
9	1.740	1872.1		1596.7
10	1.724	1836.8	1.710	1479.9
11	1.703	1801.1	1.653	1371.4
12	1.683	1764.8	1.595	1276.3
13	1.663	1728.1	1.545	1196.3
14		1691.1	1.494	1126.6
15	1.62	1653.5	1.452	1067.1
16	1.593	1615.4	1.404	1015.5
17	1.572	1576.8		966
18		1537.3		922
19	1.522	1497.7		882
20	1.500	1458.2		845
21	1.475			810
22			1.188	775
23				744
24				717.7
25				690.3
26			1.063	661.8
27			1.036	637.6
28				607.4
29			.977	

D. DISCUSSION OF RESULTS

Fig. 3 shows the values of $\Delta G_{v+\frac{1}{2}}$ plotted against v for both the $B^2\Sigma_u^+$ and the $X^2\Sigma_g^+$ state. In each case the dotted portion of the curve corresponds to the part of the curve that is extrapolated beyond the observed values to the dissociation limit. If one assumes that the potential curves of the molecule have no maxima then the areas under a $\Delta G_{v+\frac{1}{2}}$ curve correspond to the energy necessary to dissociate a molecule in a particular electronic state into two atoms each in the electronic state that results from the dissociation under consideration. The problem of the determination of the heat of dissociation of the N_2^+ molecule therefore resolves itself into a matter of making an accurate estimate of the area under the ΔG curve and the determination of the electronic state of the atoms that result from the dissociation.

The vibrational levels of the ground state can be observed up to $v = 21$, this level being 38,411 cm.$^{-1}$ above $v = 0$. The extrapolation of the $\Delta G_{v+\frac{1}{2}}$ curve for this state is quite a long one and therefore not very accurate. If the equation for the vibrational levels, given above, is used to make the extrapolation then the dissociation energy is found to be about 60,000 cm.$^{-1}$ As

discussed previously the dissociation energy of N_2^+ is known to be either 70,358 cm.$^{-1}$ or 51,131 cm.$^{-1}$ It would require only a small change in the curvature of the curve to bring the above result up to 70,358 cm.$^{-1}$, but it would require a sudden change in the curvature to obtain an area of 51,131 cm.$^{-1}$
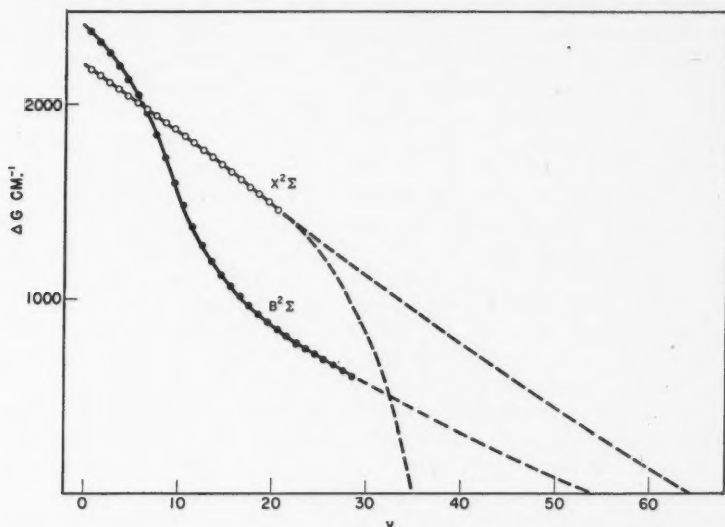

FIG. 3. ΔG_v curves for the $B^2\Sigma_u^+$ and for the $X^2\Sigma_g^+$ states of N_2^+.
    The known points are indicated by circles and joined by solid lines. Even though some of the vibrational levels have not been observed (see Fig. 1), none of these points should be in error by more than a few cm.$^{-1}$ The broken portions of the curves are obtained by extrapolation. The curve of the $B^2\Sigma_u^+$ state is extrapolated so that the dissociation limit of the state is at 70,358 cm.$^{-1}$ The curve for the $X^2\Sigma_g^+$ state is extrapolated in two ways, the first corresponding to a dissociation energy of 51,131 cm.$^{-1}$ and the second corresponding to a dissociation energy of 70,358 cm.$^{-1}$

The vibrational levels of the upper state can be observed up to $v = 29$ and this corresponds to an energy of 38,214 cm.$^{-1}$ above $v = 0$ of the $B^2\Sigma_u^+$ state. A relatively short extrapolation gives 47,000 cm.$^{-1}$ for the dissociation energy of this state. Since the vibrational levels do not converge in a regular way, the method used to extrapolate the curve is to a certain extent arbitrary, but the value given above should be correct to within a few thousand cm.$^{-1}$ Since the B state is 25,566 cm.$^{-1}$ above the ground state, this convergence limit appears to be 72,500 cm.$^{-1}$ above the ground state. It is known that there is a dissociation limit 70,358 cm.$^{-1}$ above the ground state (see Fig. 1) and there seems little doubt but that the B state does dissociate into this limit.

The Wigner and Witmer correlation rules show that a nitrogen atom in the ^4S state and a nitrogen ion in the ^3P state give rise to a $^2\Sigma_u^+$ and a $^2\Sigma_g^+$ state of the N_2^+ molecule. If one assumes that these two states are identical with the observed $B^2\Sigma_u^+$ and $X^2\Sigma_g^+$ states, then, from the fact that the $B^2\Sigma_u^+$ state

does have a limit 70,358 cm.$^{-1}$ above the ground state, it follows at once that the true heat of dissociation of N_2^+ is 70,358 cm.$^{-1}$ As mentioned above it is quite possible to make the $\Delta G_{v+\frac{1}{2}}$ curve for the ground state lead to this value for the dissociation energy. Therefore this value for the dissociation energy is consistent with all the observed data and leads to no difficulties in the interpretation of the spectrum of N_2^+.

If, on the other hand, one assumes that the heat of dissociation of N_2^+ is 51,131 cm.$^{-1}$ then it follows that the $B^2\Sigma_u^+$ state must dissociate into a nitrogen atom in the ^2D state and a nitrogen ion in the ^3P state. Below this dissociation limit there exists one in which the nitrogen atom is in a ^4S state and the ion is in the ^1D state, and a second limit in which both the atom and the ion are in their ground states ($^4S + {}^3P$). The first of these limits ($^4S + {}^1D$) does not give any $^2\Sigma^+$ states and is therefore not important in this discussion. The second limit, $^4S + {}^3P$, does give a $^2\Sigma_u^+$ and a $^2\Sigma_g^+$ state. Assuming then that the dissociation energy of N_2^+ is 51,131 cm.$^{-1}$, it follows that the $^2\Sigma_u$ potential energy curve arising from normal atoms must cross the observed $B^2\Sigma_u^+$ curve. It is almost certain that such an intersection would have to take place below the observed $v = 29$ level of the $B^2\Sigma_u^+$ state since it is highly improbable that the state arising from normal atoms could be sufficiently repulsive to rise above this level. One may assume that the interaction between the two states is small and the $^2\Sigma_u^+$ state arising from normal atoms crosses and possibly predissociates the $B^2\Sigma_u^+$ state at some point between $v = 16$ and $v = 22$ where none of the vibrational levels have been observed. The vibrational levels $v = 22$ and above must then be considered as being sufficiently far above the point of predissociation that they are not appreciably affected by it. The $X^2\Sigma_g^+$ state can be correlated with the atomic states in two ways. First one may assume that the dissociation limit of the X state is the same as for the B state, that is the dissociation products are a nitrogen atom in a ^2D state and an ion in a ^3P state. One must then assume that the $^2\Sigma_g^+$ state arising from normal atoms interacts with the observed X state only at energies higher than any of the observed levels. Alternatively one may assume that the $X^2\Sigma_g^+$ state dissociates into normal atoms and the $B^2\Sigma_u^+$ state goes into atoms in the $^2D + {}^3P$ states. This corresponds to extrapolating the $\Delta G_{v+\frac{1}{2}}$ curve (Fig. 3) for the ground state so that the area under the curve is 51,131 cm.$^{-1}$ which, as was discussed earlier, is possible but leads to a sudden change in the curvature of the curve.

It is also possible to obtain some information regarding the dissociation energy of N_2^+ from the $^2\Pi$ state of the molecule. The $^2\Pi$ state was first found from a study of the perturbations in the B state (1). More recently bands due to transitions from the low vibrational levels of the $^2\Pi$ state to the ground state have been observed (10, 5). It is gratifying to find that the value of $\omega_e x_e$ and the positions of the vibrational levels predicted from the perturbations agree well with those that can be found by an extrapolation of the observed levels and it can be shown that it is the $v = 10$ level of the $^2\Pi$ state that perturbs the $v = 0$ level of the $B^2\Sigma_u^+$ state.

The vibrational levels of the $^2\Pi$ state have been traced up to $v = 29$ by Brons (1). These vibrational levels do not converge to a dissociation limit at 51,131 cm.$^{-1}$ but may converge to a limit at 70,358 cm.$^{-1}$ Unfortunately the large energy gaps between observed perturbations together with the fact that one cannot determine exactly the positions of the vibrational levels that cause the perturbation make it possible that the vibrational numbering given by Brons is incorrect and therefore one cannot be certain about the dissociation limit of the $^2\Pi$ state.

It is of interest to consider whether one can determine the reason for the unusual shape of the $\Delta G_{v+\frac{1}{2}}$ curve of the $B^2\Sigma_u^+$ state. If one considers that the
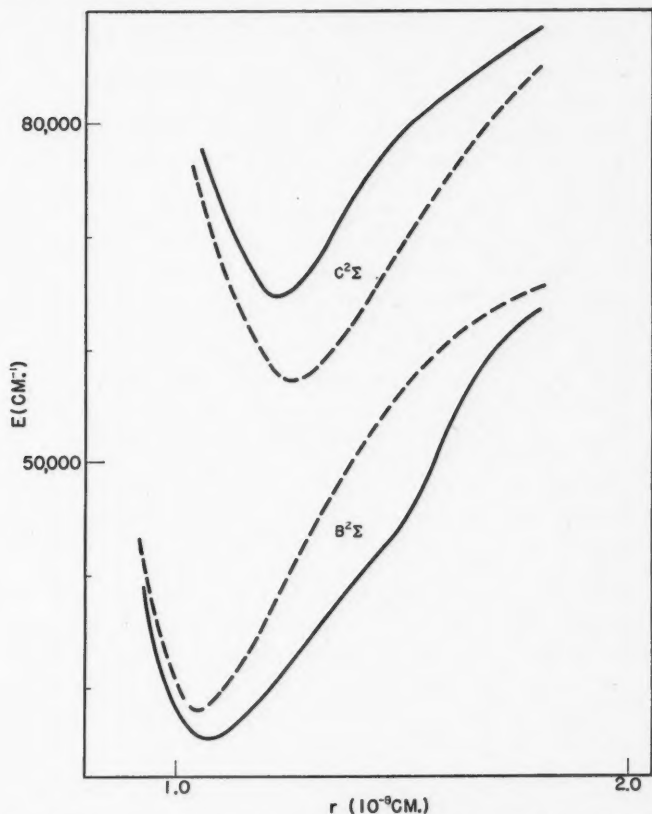

FIG. 4. Potential curves to illustrate the interaction between the $C^2\Sigma$ and the $B^2\Sigma$ states of N_2^+.

The dotted lines indicate the positions the potential curves would have if there were no interaction between the two states. The solid curves indicate the actual positions of the potential curves. These curves are schematic only.

unusual shape of the $\Delta G_{v+\frac{1}{2}}$ curve is due to an unusual shape of the potential curve of this state it is rather natural to assume that the cause lies in an interaction between two states. The interaction must be a strong one and therefore cannot be related to the intersection of the $B^2\Sigma_u^+$ curve by one from a lower dissociation limit since, as discussed previously, if such an intersection does occur, it must occur with a weak interaction between the two states. It does however seem possible that the unusual behavior is caused by an interaction between the $B^2\Sigma_u^+$ state and the $C^2\Sigma_u^+$ state. The minimum of the C state is at a larger internuclear distance than that of the B state and if the interaction is such as to cause an apparent repulsion of the potential curves the result will be a distortion of the lower potential curve. This effect is shown schematically in Fig. 4 in which the dotted lines represent the unperturbed potential curves and the solid lines the perturbed curves. It can be seen from the curves that the effect of the perturbation is such as to cause the $B^2\Sigma_u^+$ state to flatten out in the middle of its energy range and hence cause the values of ΔG to decrease rapidly in this region. The displacement of the $C^2\Sigma_u$ state may not have any marked effect on the low ΔG values of that state, but it does effectively move the minimum to a smaller internuclear distance. Thus the B values of the first few vibrational levels of the $C^2\Sigma$ state should be anomalously large. Such an effect has indeed been observed by Setlow (12), thus tending to confirm this interpretation of the anomalous ΔG curve of the B state.

It has been noted by Watson and Koontz that the $v = 3$ level of the $C^2\Sigma_u^+$ state appears to have an anomalously high population when observed in a discharge through helium containing a little nitrogen. They attribute this to the fact that the energy of the $v = 3$ level of the C state is almost equal to the ionization potential of helium. This effect may also be interpreted in a different manner. The $v = 3$ level is just 280 cm.$^{-1}$ above the asymptote of the $B^2\Sigma_u^+$ state. It is then possible that a nitrogen ion and a nitrogen atom coming together at this dissociation limit may undergo a radiationless transition into the $v = 3$ level of the C potential curve. If we have a gas in a discharge tube which contains a large number of nitrogen ions and atoms then by this process of inverse predissociation we might expect the $v = 3$ level to be highly populated. On the other hand if we are dealing with a source in which the $C^2\Sigma_u^+$ state is excited from the ground state by electron collision and there are only very few ions and atoms present then we should expect the C state to be predissociated at the $v = 3$ level. This state has not been investigated sufficiently well to know whether such a predissociation actually exists.

E. CONCLUSION

The value of the heat of dissociation of N_2^+ and hence of N_2 cannot be definitely determined from the known spectrum. There is no doubt however that the observed spectrum can be interpreted much more simply if one assumes the higher value (70,358 cm.$^{-1}$) for the dissociation energy of N_2^+. An extrapolation of the observed levels of the ground state, the observed levels of the $B^2\Sigma_u$ state, and the perturbation of the $B^2\Sigma_u$ state each independently points to the higher value. It is perhaps interesting to note that the problem

faced here is one common to most discussions of the determination of dissociation energies from spectroscopic data. Though it is certain that molecular states of the same symmetry cannot cross in the sense that for a certain internuclear distance a true degeneracy exists, it is nevertheless possible to conceive of an interaction sufficiently small so that, from the point of view of the observed spectra, we can say that two states of the same symmetry do cross. Once one assumes that such apparent crossings do take place there is seldom any certain way of correlating observed molecular states with the molecular states known to arise from given pairs of atoms and with few exceptions molecular spectra can give, with certainty, only an upper limit to the dissociation energy.

A review of the spectroscopic data for nitrogen and related molecules shows that much of it can be interpreted equally well by assuming either 78,717 or 59,490 cm.$^{-1}$ for the dissociation energy of N_2. There are however certain facts that require the introduction of unusual assumptions in order to be consistent with a given value of the dissociation energy. Thus, prior to this work, if one assumed the higher value for the dissociation energy one was forced arbitrarily to assume that the potential curve of the B state of N_2^+ did have an anomalous shape that allowed it to dissociate at 70,358 cm.$^{-1}$ Now it has been shown that such an anomalous curve does indeed exist. As pointed out in a previous publication (6) the assumption of the higher value of the dissociation energy requires that the $^5\Sigma_g^+$ state of N_2 resulting from normal atoms be stable and that this $^5\Sigma_g^+$ predissociate the $a^1\Pi_g$ state. As was indicated in that publication and later emphasized by Prof. R. S. Mulliken in private discussions, there is no sound theoretical reason why these conditions cannot be fulfilled. Therefore I believe that there now exist no spectroscopic data that cannot be interpreted simply if one assumes 9.756 ev. for the dissociation energy of N_2. On the other hand, the assumption of the lower value for the dissociation energy requires the assumption of anomalous shapes for the potential curves and anomalous interactions between potential curves not only for N_2^+ but also for NO and N_2. Thus it appears that spectroscopic evidence favors the value of 9.756 ev. for the dissociation energy of N_2.

REFERENCES

1. BRONS, H. H.   Physica, 1: 739.   1933.
2. CHILDS, W. H. J.   Proc. Roy. Soc. (London), A, 137: 641.   1932.
3. COSTER, D. and BRONS, H. H.   Z. Physik, 73: 747.   1932.
4. CRAWFORD, F. H. and TSAI, P. M.   Proc. Am. Acad. Arts Sci. 69: 407.   1935.
5. DALBY, F. W. and DOUGLAS, A. E.   Phys. Rev. 84: 843.   1951.
6. DOUGLAS, A. E. and HERZBERG, G.   Can. J. Phys. 29: 294.   1951.
7. HAGSTROM, HOMER D.   Revs. Modern Phys. 23: 185.   1951.
8. HERZBERG, G.   Ann. Physik, 86: 189.   1928.
9. KISTIAKOWSKY, C. B., KNIGHT, H. T., and MALIN, M. E.   J. Am. Chem. Soc. 72: 2972.   1951.
10. MEINEL, A. B.   Astrophys. J. 114: 431.   1951.
11. PARKER, A. E.   Phys. Rev. 44: 90, 914.   1933.
12. SETLOW, R. B.   Phys. Rev. 74: 153.   1948.

RADIAL MATRIX ELEMENT FOR THE QUADRUPOLE TRANSITION WITH THE MORSE POTENTIAL[1]

By H. A. Buckmaster

ABSTRACT

A general formula for the radial part of the matrix element for the quadrupole transition with the Morse potential is derived using standard methods of analysis. The same methods can also be used to derive an expression for the radial part of the dipole transition matrix element.

INTRODUCTION

The Morse potential (6),

$$(1) \qquad V(r) = D[e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}],$$

has been successfully used for the interpretation of the spectra of diatomic molecules when the effect of rotation is neglected (2). The radial part of the matrix element for the dipole transition (M_D) with the Morse potential has been previously calculated by Wu (7) and Mizushima (5) when $m = 0$ and $n = 1, 2$, and 3. These special cases agree with the general formula given by Infeld and Hull (3). The same general result may be obtained by the method of the present paper. M_D can be expressed in the form

$$(2) \qquad M_D = \frac{(-1)^{n+m+1}}{a(n-m)(n-m+b)}\left[\frac{n!\Gamma(n+b+1)\cdot b\cdot b'}{m!\Gamma(m+b'+1)}\right]^{\frac{1}{2}}, \qquad m < n$$

where $b' = 2d - 2m - 1$.

QUADRUPOLE MATRIX ELEMENTS

To calculate the radial part of the matrix element for the quadrupole transition (M_Q), we must evaluate the integral

$$(3) \qquad M_Q = \int_0^\infty \overline{R_m(r)}\, r^2 R_n(r)dr.$$

In order to obtain a closed expression for M_Q with the Morse potential, we must change the limits of integration from $(0, \infty)$ to $(-\infty, \infty)$. D. ter Haar (1) has shown that this change is, in general, justifiable. For the Morse potential, the eigenfunctions are given in Ref. (6) by

$$(4) \qquad R_n(r) = N_n e^{-z/2} z^{b/2} L_{n+b}^b(z)$$

where

$$z = 2de^{-a(r-r_e)}, \qquad N_n = \left[\frac{a\cdot b\cdot n!}{\Gamma(n+b+1)}\right]^{\frac{1}{2}} e^{i\pi b},$$

$$d = \frac{2\pi(2\mu D)^{\frac{1}{2}}}{ah}, \qquad b = 2d - 2n - 1,$$

and $\qquad L_{n+b}^{b}(z) = \sum_{l=0}^{n} \binom{n+b}{n-l} \frac{(-z)^{l}}{l!}$,

(5) $\qquad \binom{n+b}{n-l} = (n+b)(n+b-1) \ldots (n+b-(n-l-1))$,

or

(6) $\qquad n!\, e^{-z} z^{b}\, L_{n+b}^{b}(z) = \frac{d^{n}}{dz^{n}} (e^{-z} z^{n+b})$.

Substituting the eigenfunctions of Equation (4) into Equation (3), making the change of variable

$$z = 2de^{-a(r-r_e)},$$

and simplifying yields

(7) $\qquad M_Q = \frac{N_n \overline{N_m}}{a^3} A + 2\left(\frac{\ln 2d}{a} + r_e\right) M_D$

where $\qquad A = \int_{0}^{\infty} (\ln z)^2 e^{-z} z^{(b+b'-2)/2} L_{n+b}^{b}(z) L_{m+b'}^{b'}(z) dz$

and M_D is given by Equation (2).

Using Relations (5) and (6), A becomes

(8) $\qquad A = (1/n!) \sum_{l=0}^{m} \binom{m+b'}{m-l} [(-1)^{l}/l!]\, B$

where $\qquad B = \int_{0}^{\infty} (\ln z)^2 z^p (d^n/dz^n)(e^{-z} z^{n+b}) dz$,

$$p = n - m - 1 + l, \quad \text{and } m < n.$$

Integrating B by parts p times gives

(9) $\qquad B = (-1)^p p! [C + 2(\psi(p) + \gamma) D]$

where $\qquad C = \int_{0}^{\infty} (\ln z)^2 \frac{d^{m-l+1}}{dz^{m-l+1}} (e^{-z} z^{n+b}) dz$,

$$D = \int_{0}^{\infty} \ln z \frac{d^{m-l+1}}{dz^{m-l+1}} (e^{-z} z^{n+b}) dz,$$

$$\gamma \equiv \text{Euler's constant},$$

and $\qquad \psi(z) = (d/dz)\ln\Gamma(z+1) = -\gamma + \sum_{i=1}^{\infty} (1/i - 1/(z+i))$.

The values of $\psi(z)$ are tabulated in Jahnke and Emde (4). When z is a positive integer n,

$$\psi(n) = -\gamma + \sum_{i=1}^{n} 1/i.$$

Integrating C and D by parts $(m-l+1)$ times gives

$$(10) \qquad C = 2(m - l)!\Gamma(2d + l - n - m - 1)$$

$$\times \left[\psi(m - l) - \psi(2d + l - n - m - 2) + \gamma\right],$$

$$(11) \qquad D = - (m - l)!\Gamma(2d + l - n - m - 1).$$

By Equations (8), (9), (10), and (11), Equation (7) becomes

$$M_Q = \frac{2(-1)^{n+m+1}}{a^2}\left[\frac{m!\Gamma(m + b' + 1)\cdot b\cdot b'}{n!\Gamma(n + b + 1)}\right]^{\frac{1}{2}}$$

$$\times \sum_{l=0}^{m}\frac{\Gamma(2d + l - n - m - 1)\Gamma(n - m + l)}{\Gamma(l + 1)\Gamma(2d - 2m + l)}$$

$$\times \left[\psi(m - l) - \psi(n - m - 1 + l) - \psi(2d + l - n - m - 2)\right]$$

$$(12) \qquad\qquad + 2\left(\frac{\ln 2d}{a} + r_e\right)M_D, \qquad\qquad m < n$$

which is the desired result.

ACKNOWLEDGMENT

REFERENCES

1. TER HAAR, D. Phys. Rev. 70: 222. 1946.
2. HERZBERG, G. Spectra of diatomic molecules. 2nd ed. D. Van Nostrand Co., Inc., New York. 1950.
3. INFELD, L. and HULL, T. E. Revs. Modern Phys. 23: 21. 1951.
4. JAHNKE, E. and EMDE, F. Tables of functions. 4th ed. Dover Publications, New York. 1945.
5. MIZUSHIMA, L. Phys. Rev. 77: 150. 1951.
6. MORSE, P. M. Phys. Rev. 34: 57. 1929.
7. WU, T. Y. Vibrational spectra and structure of polyatomic molecules. National University of Peking, Kun-Ming, China. 1939.

DESIGN AND OPERATION OF A 'MEAN DEVIATION METER'[1]

By L. H. Greenberg[2] and W. W. Happ[3]

ABSTRACT

An instrument was constructed and calibrated to measure the mean deviation of the counting rate from a series of pulses that are not uniformly spaced. Two resistance–capacitance 'memory' circuits measure the instantaneous and the average counting rates. A rectifier bridge circuit is used to compute the relative deviation. Over a large part of the range the response is linear and reproducible within 5% for full scale deflection. The instrument is used in conjunction with the counting of radioactive radiations; other uses are discussed.

1. INTRODUCTION

Purpose

An electronic instrument is described, which measures the statistical properties of a series of pulses arriving at irregular intervals. A typical example would be the distribution of spacings between consecutive nuclear disintegrations. Since particles from a radioactive source are emitted independently at random intervals, successive counts should follow a Poisson distribution (2, 3) if detected and recorded by an ideal counting mechanism. Any deviation from the theoretical distribution will yield information on processes that interfere with, or modify, the original distribution of pulses.

Standard Deviation

For a given counting rate, marked changes of the standard deviation may be observed and are attributed to defects in the counting mechanism (1, 3, 8) such as:

(a) 'Dead time', denoting the interval following each pulse during which no additional pulse is accepted.

(b) Pick up of stray pulses, frequently caused by insufficient shielding from 60-cycle line frequency.

(c) Intermittent counting due to fluctuating voltage on the anode of a Geiger counter.

(d) Two or more pulses recorded for one pulse entering the counter.

The instrument described may be used to detect these defects.

Statistical Reliability

The statistical reliability of counts from a radioactive source is usually determined by the 'Chi Square' test (5), which requires a large number of

---

readings and lengthy calculations. Moreover, when the Chi Square test is used the reliability is not known until long after the readings have been taken. If subsequently the results are shown to be erroneous, valuable time may be lost and in some cases it may not be possible to repeat the measurements. Also, to obtain a satisfactory estimate of the reliability requires a much longer series of readings than to obtain only an estimate of the counting rate. Consequently, there is a tendency among workers to disregard this step completely or to use a short series of measurements which may give a standard deviation within the range expected by random sampling, but which may be found to be significantly different, if a longer series of readings is taken.

The instrument to be described in this paper makes it possible to detect deviations from the expected distribution at a glance and while observations are being taken.

Counting Rate

The number of pulses occurring during a time interval divided by this interval is the counting rate and in particular:

M is the average counting rate, if the time interval is much larger than the mean spacing between pulses.

x is the instantaneous counting rate, if the time interval is of the same order of magnitude as the pulse spacing.

Information on the statistical distribution of pulse spacings is obtained by comparison of M and x. Either the mean deviation $\overline{|M-x|}$ or the standard deviation $[\overline{(M-x)^2}]^{\frac{1}{2}}$ can be used to estimate the reliability of data.

2. PRINCIPLE OF OPERATION

Average Counting Rate

To obtain the average counting rate a counting rate meter was used that consisted essentially of a circuit designed by Kip *et al.* (6). Pulses of almost any voltage shape and varying magnitude were suitably amplified to actuate a uniform pulse generator. The uniform pulses were fed into a resistance–capacitance circuit, which is at times referred to as an "RC tank". Schiff and Evans (9) made a statistical analysis of this integrating circuit and showed that the instrument is an averaging mechanism with an "exponential decaying memory". The average time interval over which each pulse is "remembered" is equal to RC. The average number of pulses stored is therefore MRC; hence the larger this number the more pronounced will be the averaging or smoothing action of the RC tank.

Instantaneous Counting Rate

To obtain the deviation from the mean, two of the above mentioned memory circuits are required. One circuit measures the average counting rate M, the other circuit measures the instantaneous counting rate, x, by using different
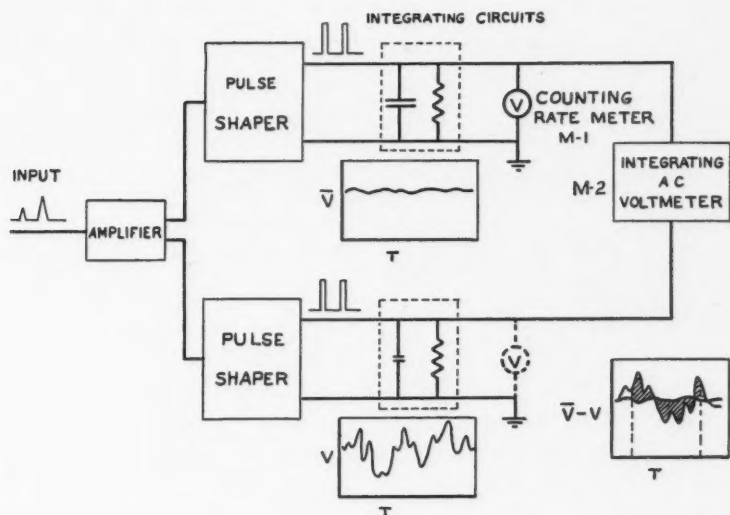
Fig. 1. Block diagram of the Mean Deviation Meter, showing voltage variations in different parts of the circuit.

'memory' time constants. Fig. 1 shows how the voltage may vary in each circuit. The shaded area between the two curves gives the deviation of the actual counting rate from the mean.

Mean Deviation

Both integrating circuits are designed to produce the same average voltage so that the instantaneous voltage difference gives a reading $|x - M|$. The mean of the absolute value of this voltage difference is obtained by using a full wave rectifier followed by an RC smoothing circuit. The values of $\overline{|M - x|}$ and M are then read from a suitably calibrated voltmeter or from a recording potentiometer.

Standard Deviation

By using a high resistance RMS a-c. voltmeter, such as a hot wire instrument, $(x - M)^2$ could be obtained. When averaged this would give a direct indication of the standard deviation for any frequency distribution. Because of the difficulty in obtaining the long time constants desired and also because the recording potentiometer available could only be used with d-c. voltage, it was found more convenient to use the mean deviation.

3. STATISTICAL CONSIDERATION

Mean Deviation

The instrument is designed to obtain a voltage proportional to the mean deviation (δ) of the counting rate.

Since standard deviation is more generally used, the instrument was calibrated to read the standard deviation (σ) of the counting rate.

The use of σ in place of δ is rigorously justified (4) for normal distribution for which

$$\frac{\delta}{\sigma} = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} = 0.798 .$$

For the Poisson distribution

$$\frac{\delta}{\sigma} = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \left(1 - \frac{1}{12\ MRC}\right)$$

where MRC is the number of pulses stored in the condenser; this relation is accurate within about 1% for $MRC > 1$. In this instrument RC is chosen to satisfy this condition.

Standard Deviation

The standard deviation of the counting rate M, measured over a time interval T_m, is given by

$$\sigma_m = \left(\frac{M}{T_m}\right)^{\frac{1}{2}} .$$

The value of T_m is dependent only on the instrument, since it is the interval over which the meter effectively averages the counting rate.

On the other hand the meter is calibrated by counting the number of pulses in a fixed time interval T_c which is not equal to T_m. Then the standard deviation in the observed number of pulses is

$$\sigma_c = (MT_c)^{\frac{1}{2}} .$$

Eliminating M, this yields

$$\sigma_c T_c^{-\frac{1}{2}} = \sigma_m T_m^{\frac{1}{2}} = \beta .$$

Now β can be calculated because σ_c and T_c are known. Since β is independent of the time interval used in the calibration, it is used to correlate the deflection of the meter with the calculated standard deviation of the counting rate. For calibration purposes no generality is lost, if T_m is assumed to be equal to unity.

A detailed analysis of statistical problems associated with this instrument is given in a companion paper (4).

4. CHOICE OF CIRCUIT ELEMENTS

The circuit diagram for the instrument is given in Fig. 2; the components are listed in Table I.
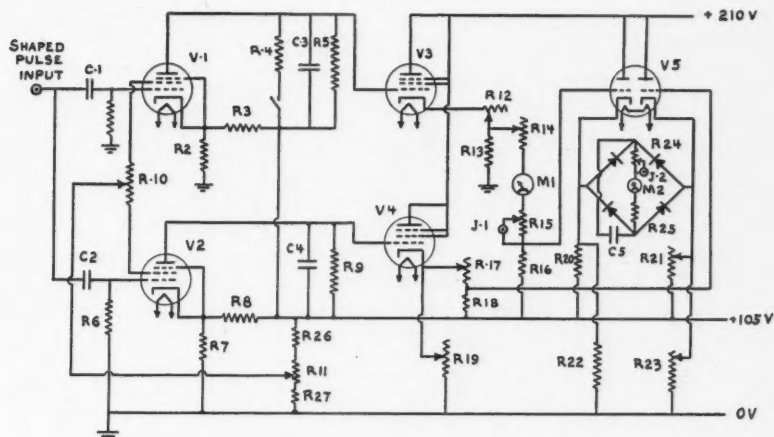

FIG. 2.   Circuit diagram of the Mean Deviation Meter.

TABLE I

LIST OF COMPONENTS
Resistances in ohms.   Capacities in microfarads.

*V*1, 2:	6SJ7		*R*20, 27:	5000 1 watt
*V*3, 4:	6AC7—1852		*R*22:	25,000 1 watt
*V*5:	6C8		*R*25:	15,000 ½ watt
*R*1, 6:	0.5 meg. ¼ watt		*R*26:	75,000
*R*2, 7:	3500 10 watt			
*R*3, 8:	30,000 1 watt		*M*1:	0–5 ma.
			*M*2:	0–100 ma.
*R*4:	100,000 ½ watt			
*R*5, 9:	30 meg. ¼ watt		*C*1, 2:	0.0002
*R*10, 14, 17, 21, 23, 24: 5000 pot.			*C*3:	2.0
			*C*4:	0.0188 mica
*R*11:	15,000 pot.		*C*5:	2000 50v.
*R*12:	500 pot.			Mallory 2–44: 161, 511.
*R*13:	12,000 10 watt		*C*6:	0.1
*R*15:	50 pot.			
*R*16, 18: 2000 ½ watt				
*R*19:	10,000 10 watts variable plus 500 pot.			

Circuit elements for the standard deviation circuit were chosen to fulfill the following requirements:

(a) The average voltage on both integrating tank circuits should be the same, since $\bar{x} = \bar{M}$. The difference in voltage should measure $(x - M)$.

(b) The average voltage difference between the two circuits should be as large as possible provided the instantaneous rate does not exceed the average rate by an amount which would put it on a nonlinear region of the vacuum tube voltmeter.

(c) The counting rate indicated by M-1 should not be disturbed in reading the standard deviation because M is usually the most important quantity.

These conditions were met as follows:

(a) The average voltage on the tank condenser is given by $\bar{V} = M q R$ where q is the charge per pulse and (Mq) is the average current. If the charge per pulse q and the leakage resistance R in the two circuits were made the same, the average voltage would then be the same. Therefore, R-5 was made equal to R-9. The charge q was made the same by feeding the pulse from the multivibrator to two amplifiers, one for each section. The relative sizes of the pulses were controlled by adjustment of the relative screen grid voltages.

(b) The average voltage difference between the two circuits can be computed from the difference in standard deviations. For random counts the standard deviation in voltage V_σ has been shown (9) to be:

$$V_\sigma{}^2 = \overline{(\bar{V} - V)^2} = \frac{\bar{V}^2}{2MRC}.$$

$\bar{V}$, M, and R will be the same in the two circuits, and if the subscripts 1 and 2 refer to the circuits for M and x respectively, the voltage difference will be:

$$V_\sigma = (V_{\sigma 2}{}^2 - V_{\sigma 1}{}^2)^{\frac{1}{2}} = \bar{V}(2MR)^{-\frac{1}{2}}\left(\frac{1}{C_2} - \frac{1}{C_1}\right)^{\frac{1}{2}}.$$

If $C_1 = C_2$, then $V_\sigma = 0$ as expected; in the instrument under consideration $C_1 \gg C_2$, thus

$$C_2 = \frac{1}{2MR}\left(\frac{\bar{V}}{V_\sigma}\right)^2.$$

Now M varies as $\bar{V}$, and it is therefore permissible and desirable to make $V_\sigma = \bar{V}^{\frac{1}{2}}$. Then

(1) $$C_2 = \frac{\bar{V}}{2MR} .$$

The instrument here was designed for a full scale deflection at 5000 counts per minute and $\bar{V}$ for full scale deflection was measured to be 12.5 volts. Other ranges could be added by switching to appropriate values of C_2.

(c) The voltages at the cathodes of the tubes V-3 and V-4, Fig. 2, can be used to measure M and x. A voltmeter connected to these points would draw a noticeable current through M-1 and therefore disturb the counting rate reading. This was prevented by using a vacuum tube voltmeter drawing no current. The two voltages were fed to the grids of the double triode V-5.

These voltages were varying from 105 to about 95 volts. The cathode bias resistors were chosen to make the grids about 1 volt negative with no current in *R*-17. The voltages at the cathodes then indicated *M* and *x*.

The difference in cathode voltage was indicated by *M*-2. The absolute value of the difference was obtained by the use of a copper oxide rectifier. The condenser *C*-5 across the voltmeter was chosen to give a time constant of approximately 30 sec. The voltage difference was often about 1.5 volts. A meter with full scale deflection of 100 μa. would require a resistance of 15,000 ohms. Then to give a time constant of about 30 sec., *C* had to be 2000 μf. This is ordinarily a prohibitively large capacity, but the voltage is low and such large capacities are available for low voltage.

5. CALIBRATION OF STANDARD DEVIATION METER

Zero Setting for 'No Pulse' Input

The rate meter, *M*-1, Fig. 2, was first adjusted to zero by means of *R*-12. The voltage on the left grid of *V*-5 was then 105 volts. *R*-20 was chosen to make the cathode relatively negative by about 1 volt at this adjustment. *R*-19 was then adjusted to give an equal potential on the other grid of *V*-5. This was obtained when there was no current in *R*-17 and hence adjustment of *R*-17 produced no change on the grid and hence no change in the reading indicated by *M*-2. By adjusting *R*-23, the cathode potentials of *V*-5 were then made equal, thus reducing the current in *M*-2 to zero.

Zero Setting for a Regular Input ($\sigma = 0$)

A regular series of pulses, controlled by the 60 cycle circuit, was fed into the meter and the meter was allowed to come to equilibrium. The sizes of the pulses fed on to the tank circuits were made equal by adjusting *R*-10 until a minimum was obtained in *M*-2 with *M*-1 indicating the correct counting rate. The scale deflection for the counting rate was adjusted by varying the grid voltage with *R*-11. Finally a minimum was obtained in *M*-2 by adjustment of *R*-21. A true zero could not be obtained because of the nature of the meter.
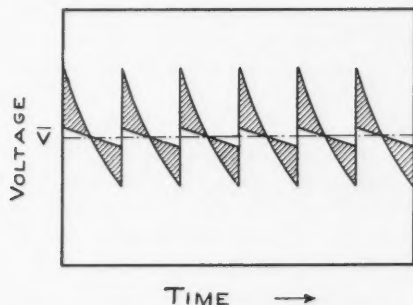

FIG. 3.   Zero reading of the Mean Deviation Meter for regular pulses.

Fig. 3 shows an exaggerated plot of the voltages on the tank condensers of the circuits with the two time constants and a regularly spaced pulse input. The shaded area gives the average of the absolute value of the voltage difference.

The accuracy of the standard deviation meter is limited by this type of zero reading, which is expected to be a function of the counting rate. This zero correction is appreciable only for small meter deflections for which it would then be a significant fraction of the indicated reading. Except for regular counts small scale deflection can be avoided by using a suitable range. The meter could be built with several ranges following the design of Kip *et al.* (6) and using Equation (1) to calculate the value of the tank condenser for the instantaneous reading of the rate.

Standard Deviation Scale Calibration

An externally quenched RCL Model 20 Geiger tube was used to detect radiations from a radium sample. Pulses were then fed simultaneously into two channels:

(i) A scaler (Atomic Inst. Co. Model 101A) followed by a mechanical register.

(ii) The mean deviation meter followed by a recording potentiometer. A calibration was obtained by comparing the readings of M-2 with the standard deviation as obtained from the number of pulses registered by the scaler in a given constant time interval. By connecting a recording potentiometer to jacks J-1 and J-2 (Fig. 2) a continuous record of the counting rate and of its standard deviation was obtained. A typical trace is shown in Fig. 4. Actually
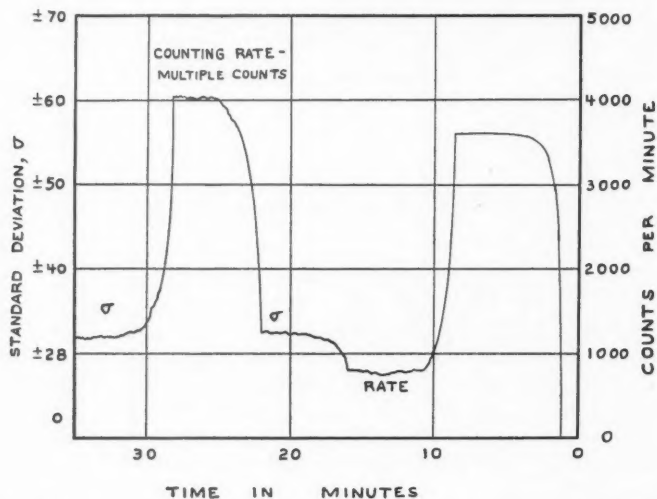

FIG. 4.   Trace from recorder alternately showing counting rate and standard deviation.

only one recorder was available and connected to read the rate and standard deviation alternately. For calibration the pulses from the counter tube were fed at the same time into a scaling circuit which was adapted for counting pulses during a series of time intervals each 15 sec. long with an accuracy of 0.1%.

The calibration curve correlating the deflection of the standard deviation meter and the calculated standard deviation β is given in Fig. 5. The standard
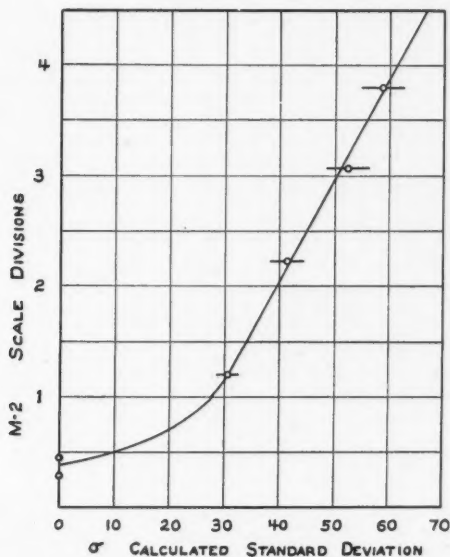

FIG. 5. Calibration curve for the Mean Deviation Meter.

error of β is equal to $(2n)^{-\frac{1}{2}}\beta$ if n is large (where n is the number of intervals used to obtain β); this standard error is shown on the same graph. To obtain each point with a standard error of 1% would have been very laborious; as a compromise approximately 100 readings per point were taken, which gave a standard error of approximately 7%.

The reproducibility of the readings was excellent. Some drift in the recorded readings, however, was observed. It was necessary when this was noticed on the trace to check on 60 cycles. The cause of the drift was located in the pulse splitting elements. Adjustment of R-10 to give a minimum in M-2 gave the correct counting rate again and the original standard deviation reading.

For this reason it is suggested that any further instruments of this type be made with two pulse shaping circuits.

6. DISCUSSION

Multiple Counts

Measurements were made using multiple pulses obtained by adjusting the shaping circuit until the multivibrator was slightly unstable and would give two or more pulses for each one entering it. Fig. 4 shows a trace for which two counting rates from the same input show the same standard deviation but different rates because of multiple counting.

From 10 to 18 min. the sample showed a rate of 900 counts per minute. The standard deviation of this rate is given from 18 to 22 min. as ± 30 counts per minute. The circuit was then made to record several pulses for each one entering and from 22 to 28 min. recorded a rate of 4000 counts per minute from the same sample. The standard deviation of this reading was recorded from 30 to 35 min. and is still ± 30 counts per minute instead of ± 63 which would be expected if the pulses were random.

To obtain a similar comparison to the same accuracy by computing the standard deviation from a series of samples would require about 1000 separate determinations of the counting rate.

Effect of Dead Time

Two types are generally considered:

(A) Each rejected pulse extends the dead time.

(B) The rejected pulse does not extend the dead time.

Feller (3) showed that an input rate M measured over an interval T with a dead time τ gives an expected number of counts m and a corresponding deviation σ :

(A) For extended dead time

$$m = MTe^{-M\tau} + 1 - e^{-M\tau}[M\tau + 1],$$

$$\sigma^2 = (MT - M\tau)(1 - 2M\tau e^{-M\tau})e^{-M\tau} - e^{-M\tau} + e^{-2M\tau}(1 + M\tau)^2.$$

(B) For nonextended dead time

$$m = \frac{MT}{1 + M\tau} + \frac{(M\tau)^2}{2(1 + M\tau)^2},$$

$$\sigma^2 = \frac{MT}{(1 + M\tau)^3}.$$

The following assumptions are almost always satisfied experimentally:

$$MT > > | > M\tau.$$

If these assumptions are made one obtains:

(A) For extended dead time $\dfrac{\sigma^2}{m} = (1 + M\tau)^{-2}.$

(B) For nonextended dead time $\dfrac{\sigma^2}{m} = 1 - 2M\tau e^{-M\tau}.$
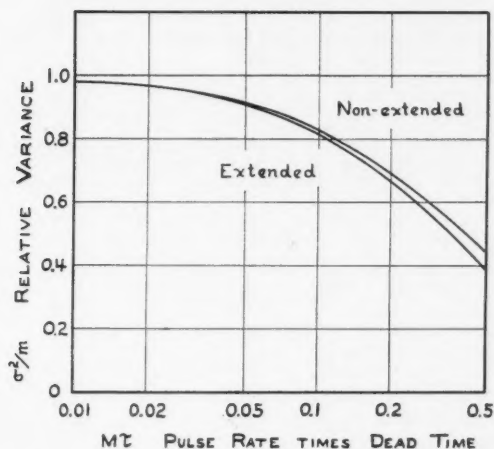
FIG. 6. Effect of dead time of a Geiger counter on the variance of the recorded rate.

Since m and σ can be readily obtained from the instrument, Fig. 6 may be used to give a measurement of the dead time if it is known to be extended or non-extended. If this is not known, measurements of σ and m could be used to give an indication of the type of dead time which may prove helpful in understanding the mechanisms of the counter.

Applications

Although the instrument is primarily intended to keep a continuous check on the counting rate in routine analyses of radioactive samples, it could readily be adapted for other purposes. In fact, it may be used wherever a statistical analysis is required of a continuously arriving flow of data, and where an accuracy of about 5% is satisfactory. Since frequently statistical measurements have an inherent uncertainty of this order of magnitude, greater accuracy is at times precluded or not desired.

The instrument may prove useful in the statistical analysis of such problems as: cosmic ray bursts, continuously recorded meteorological variations such as temperature or humidity, biometrical evaluations, variations of power requirements from hydrostations, noise variations in electronics and in acoustics, transients in power lines, and fluctuation in performance characteristics. The scope of the instrument can be extended to a large range of statistical problems by supplying the continuous flow of information from punched tape, magnetic tape, or from a Curve Computer (7).

REFERENCES

1. CLARK, C. E.   Rev. Sci. Instruments, 20: 51.   1949.
2. ELMORE, W. C.   Nucleonics, 6 (1): 26.   1950.
3. FELLER, W.   Courant anniversary volume. Interscience Publishers Inc., New York. 1948.
4. KEEPING, E. S. and HAPP, W. W.   Can. J. Phys. 30: 329.   1952.
5. KENDALL, M. G.   Advanced theory of statistics.   Griffin and Co., London.   1947.
6. KIP, A., BOUSQUET, A., EVANS, R., and TUTTLE, W.   Rev. Sci. Instruments, 17: 323.   1946.
7. MIDDLETON, W. E. K.   Optical Society of America meeting, March 11, 1950.
8. RAINWATER, L. J. and WU, C. S.   Nucleonics, 1 (2): 60.   1947.
9. SCHIFF, L. I. and EVANS, R. D.   Rev. Sci. Instruments, 7: 456.   1936.

STATISTICS OF THE MEAN DEVIATION METER[1]

By E. S. Keeping[2] and W. W. Happ[3]

ABSTRACT

The mean deviation is evaluated for a number of distributions of a Poisson or similar type, such as arise with counters, scaling circuits, and in particular with the mean deviation meter described by Greenberg and Happ. The mean deviation for some distributions is fairly readily obtainable, but for the charge on a single tank circuit and also for the difference of charges on two tanks with different decay constants it is necessary to obtain the probability density. Exact expressions for these density functions are given, and also approximations from which the mean deviation can be calculated.

1. INTRODUCTION

In the "mean deviation meter" described by Greenberg and Happ (Ref. 4) the mean deviation of a series of irregularly spaced pulses is measured. These pulses are assumed to originate at random intervals and the resulting distribution is derivable from the Poisson law.

Although the standard deviations of such distributions have been evaluated by several authors (Refs. 1, 2, 3, 9), the mean deviation has not been correspondingly treated, being generally less useful and mathematically much less convenient (Ref. 5, p. 215). However, in certain problems the mean deviation can be simply obtained and the following results may be useful.

2. MEAN DEVIATION OF THE TIME t BETWEEN A PULSE AND THE mth FOLLOWING PULSE

The density function is

$$f_m(t) = M^m t^{m-1} e^{-Mt}/(m-1)!$$

(1)
$$= M\, p(m-1;\, Mt)$$

(2)
$$\text{where } p(q;\, r) = e^{-r} r^q/q!\,,$$

the Poisson function, and M is the average counting rate. The expectation of t is m/M and the standard deviation (σ) is $m^{\frac{1}{2}}/M$. The mean deviation is

$$\delta = M\int_0^\infty |t - m/M|\, p(m-1;\, Mt)dt$$

$$= \frac{1}{M}\int_0^m (m-n)\, p(m-1;\, n)dn + \frac{1}{M}\int_m^\infty (n-m)\, p(m-1;\, n)dn$$

where $n = Mt$. Since $dp(m;\, n)/dn = (1 - n/m)\, p(m-1;\, n)$, we obtain

(3)
$$\delta = (2m/M)\, p(m;\, m).$$

By Stirling's approximation, for large m,

(4)
$$p(m; m) \approx (2\pi m)^{-\frac{1}{2}}\left(1 - \frac{1}{12m}\right)$$

so that

(5)
$$\delta/\sigma \approx (2/\pi)^{\frac{1}{2}}\left(1 - \frac{1}{12m}\right).$$

This is accurate even for $m = 1$ within about $\frac{1}{2}\%$.

3. MEAN DEVIATION OF THE NUMBER OF PULSES N IN A FIXED TIME T

The probability of N pulses is $p(N; MT)$. The expected value and the variance of N are both equal to MT. The mean deviation is

$$\delta = \sum_{x=0}^{n}(MT - x)\, p(x; MT) + \sum_{n+1}^{\infty}(x - MT)\, p(x; MT),$$

where n is the integer equal to or next below MT. This reduces to

(6)
$$\delta = 2MT\, p(n; MT)$$

so that

(7)
$$\delta/\sigma = 2(MT)^{\frac{1}{2}}p(n; MT).$$

For each integral value of MT, this function has a sharp minimum corresponding to $\delta/\sigma = 2n^{\frac{1}{2}}\, p(n; n)$. For intermediate values it rises to a maximum and falls again.

4. EFFECT OF A FINITE RESOLVING TIME ON THE MEAN DEVIATION

In a counter with a nonextended dead time τ, each pulse accepted throws the counter out of action for a time τ. If t is the time interval from a pulse to the mth following pulse, the probability density function is

(8)
$$\begin{cases} f_m(t) = 0, \ \ 0 < t < m\tau, \\ f_m(t) = M\, p(m - 1; Mt - Mm\tau), \ \ t > m\tau. \end{cases}$$

The expectation is

(9)
$$E(t) = m(\tau + M^{-1})$$

and the standard deviation is $\sigma = m^{\frac{1}{2}}/M$, as before. The mean deviation is

$$\delta = M\int_{m\tau}^{\infty}\left|t - \frac{m}{M} - m\tau\right| p(m - 1; Mt - Mm\tau)dt$$

$$= M\int_{0}^{\infty}\left|u - \frac{m}{M}\right| p(m - 1; Mu)du, \ \ u = t - m\tau,$$

(10)
$$= \frac{2m}{M}\, p(m; m).$$

The mean deviation is therefore also unaffected by τ.

The mean deviation of the number of pulses N in a time T is more complicated. The probability of exactly N pulses is given by

(11) $$p(N) = F_N(T) - F_{N+1}(T), \quad N \geqslant 1,$$

where $F_N(T)$ is the probability that the instant of the Nth registration is equal to or less than T. The case $N = 0$ is given by putting $F_0(T) = 1$. If the initial instant is immediately following registration of a pulse,

$$F_N(T) = \int_0^T f_N(t)dt$$

where $f_N(t)$ is given by (8) with N instead of m. Therefore

$$F_N(T) = \sum_{j=N}^{\infty} p(j; MT - MN\tau), \quad T > N\tau$$

(12) $$= I[(MT - MN\tau)N^{-\frac{1}{2}}; N - 1],$$

where I is the incomplete Gamma function tabulated by Karl Pearson (Ref. 8). For $T < N\tau$, $F_N(T)$ is of course zero. Molina's Tables (Ref. 6) give values of $p(q; r)$ and also of

$$P(q; r) = \sum_{s=q}^{\infty} p(s; r) = \int_0^r p(q - 1; s)ds.$$

Hence, from (11),

(13) $$E(N) = \sum_1^{n'} N \, p(N) = \sum_1^{n'} F_N(T),$$

where n' is the largest integer not exceeding T/τ.

This may be evaluated approximately by using the Laplace transform (L.T.). The L.T. of $F_N(T)$ is $[\phi_1(s)]^N/s$, where

$$\phi_1(s) = \int_\tau^\infty e^{-st}Me^{-M(t-\tau)}dt = \frac{M}{M+s}e^{-s\tau}.$$

The L.T. of $E(N)$ is therefore

$$\frac{1}{s}\frac{M}{M+s}e^{-s\tau}\frac{1 - \left(\dfrac{M}{M+s}\right)^{n'}e^{-n's\tau}}{1 - \dfrac{M}{M+s}e^{-s\tau}} = \frac{Me^{-s\tau}}{1 + M\tau}\left\{\frac{1}{s^2} + \frac{M\tau^2}{2(1 + M\tau)}\cdot\frac{1}{s} + \dots\right\}$$

approximately, so that

(14) $$\begin{cases} E(N) = 0, \quad T < \tau, \\[2mm] \text{or } = \dfrac{M(T - \tau)}{1 + M\tau} + \dfrac{M^2\tau^2}{2(1 + M\tau)^2}, \quad T > \tau. \end{cases}$$

The inverse L.T. of

$$\frac{1}{s}\left(\frac{M}{M+s}\right)^{n'}e^{-n's\tau}$$

is negligible compared with 1 for large values of n', because it consists of terms like $a^{n'}e^{-a}/(n')!$, where $a < M\tau$.

The variance of N is given by

$$\text{Var}\,(N) = \sum_0^{n'} [N - E(N)]^2 p(N)$$

$$= \sum_1^{n'} N^2 p(N) - [E(N)]^2$$

$$= \sum_1^{n'} (2N - 1)F_N - [E(N)]^2.$$

Since

$$\sum_1^{n'} (2N - 1)[\phi_1(s)]^N = \frac{\phi_1(1 + \phi_1)}{(1 - \phi_1)^2} - \frac{\phi_1^{n'+1}[(2n' + 1) - (2n' - 1)\phi_1]}{(1 - \phi_1)^2},$$

where $\phi_1 = (M/M + s)e^{-s\tau}$, we find on substituting and expanding in terms of $1/s$ that

$$\sum_1^{n'} N^2 p(N) = 0, \ \ T < \tau,$$

and

$$= \frac{M^2(T - \tau)^2}{(1 + M\tau)^2} + \frac{M(T - \tau)(1 + M^2\tau^2)}{(1 + M\tau)^3} + \frac{3M^2\tau^2}{2(1 + M\tau)^4} + \cdots$$

when $T > \tau$.

Hence from (14)

(15) $$\text{Var}\,(N) = \frac{M(T - \tau)}{(1 + M\tau)^3} + \frac{3M^2\tau^2}{2(1 + M\tau)^4}$$

$$= MT - M\tau(3MT + 1) + \frac{3M^2\tau^2}{2}(4MT + 3)$$

as far as terms of order τ^2.

The mean deviation of N is

$$\delta(N) = \sum_0^{n'} |N - E(N)| p(N)$$

$$= \sum_0^n (E(N) - N)\,p(N) + \sum_{n+1}^{n'} (N - E(N))\,p(N)$$

where n is the integer equal to or next below $E(N)$.

Therefore

$$\delta(N) = 2E(N)\sum_0^n p(N) - 2\sum_1^n N\,p(N)$$

$$= 2E(N)[1 - F_{n+1}(T)] - 2\sum_1^n F_N(T) + 2n\,F_{n+1}(T)$$

(16) $$= 2 \sum_{n+1}^{n'} F_N(T) - 2\{E(N) - n\} F_{n+1}(T).$$

Now

$$F_{n+1}(T) = 0, \quad T < (n + 1)\tau$$

(17) $$= \sum_{k=n+1}^{\infty} p(k; MT - M(n + 1)\tau), \quad T > (n + 1)\tau.$$

By using the Laplace transform of

$$\sum_{n+1}^{n'} F_N(T)$$

and noting that

$$[MT - M(n + 1)\tau] \, p(n - 1; MT - M(n + 1)\tau) = np(n; MT - M(n + 1)\tau),$$

we find that

(18) $$\sum_{n=1}^{n'} F_N(T) = 0, \quad T < (n + 1)\tau,$$

or

$$= n \, p(n; MT - M(n + 1)\tau)$$

$$+ \left\{ \frac{M(T - \tau)}{1 + M\tau} + \frac{M^2\tau^2}{2(1 + M\tau)^2} - n \right\} \sum_{k=n}^{\infty} p(k; MT - M(n + 1)\tau)$$

when $T > (n + 1)\tau$.

Then, from (14), (16), (17), and (18) we obtain finally

(19) $$\delta(N) = 2 \, E(N) \, p(n; MT - M(n + 1)\tau)$$

provided $T > (n + 1)\tau$. Since $n = MT - \theta$ where $0 \leqslant \theta < 1$, this merely means that $T > (1 - \theta)\tau/(1 - M\tau)$ and $M\tau$ will usually be small compared with 1.

For small values of τ,

$$p(n; MT - M(n + 1)\tau) = p(n; MT) \left[1 + (n + 1) \frac{\tau}{T} (MT - n) \right.$$

$$\left. + \frac{(n + 1)^2 \tau^2}{2T^2} \{(MT - n)^2 - n\} + \ldots \right]$$

so that

$$\frac{\delta(N)}{E(N)} = 2p(n; MT) \left[1 + (n + 1) \frac{\tau}{T} (MT - n) \right.$$

(20) $$\left. + \frac{(n + 1)^2 \tau^2}{2T^2} \{(MT - n)^2 - n\} \right]$$

as far as terms of order τ^2.

5. THE COUNTING RATE METER WITH REGULARLY SPACED INPUT

We suppose that pulses of charge q are fed into a tank at a uniform rate M, the decay constant being $RC = l^{-1}$. If $t = 0$ coincides with the arrival of a pulse and if pulses have been arriving for a long time before $t = 0$, then the total charge Q at time t is given by

$$Q = q\sum_{k=0}^{\infty} e^{-l(t+kM^{-1})}$$

(21)

$$= qe^{-lt}(1 - e^{-l/M})^{-1}, \quad 0 < t < M^{-1}.$$

Schiff and Evans (Ref. 9) have shown that this state is practically reached if the time during which pulses have been arriving is at least equal to $[\log_e (2Ml^{-1})]/2l$.

It follows from (21) that the mean value of Q over the time M^{-1} between pulses is

(22) $\bar{Q} = aq, \quad a = M/l,$

and that the variance of Q is

(23) $$\overline{(Q - \bar{Q})^2} = a^2q^2\left[\frac{1}{2a}\coth\left(\frac{1}{2a}\right) - 1\right].$$

For large values of a, this expression is approximately equal to $q^2/12$.

The average value of $|Q - \bar{Q}|$ is given by

$$M\int_0^T (\bar{Q} - Q)dt + M\int_T^{M^{-1}} (Q - \bar{Q})dt,$$

where T is the value of t for which $Q = \bar{Q}$, i.e.

(24) $$e^{-lT} = \frac{M}{l}(1 - e^{-l/M}) = a(1 - e^{-1/a}).$$

On carrying out the integrations we find that the mean deviation of Q over the interval M^{-1} is given by

$$\delta(Q) = 2\bar{Q}a\left[\frac{1}{a}(1 - e^{-1/a})^{-1} + \log a + \log(1 - e^{-1/a}) - 1\right]$$

(25) $$= 2qa^2(e^{lT} - lT - 1).$$

If a is large, MT is approximately equal to $\frac{1}{2} + 1/8a$, and $\delta(Q)$ to $\bar{Q}/4a = q/4$.

6. THE COUNTING RATE METER WITH RANDOM INPUT

If M is the average counting rate, the probability of arrival of a pulse in the interval dt is $M\, dt$. The contribution to the total charge Q on the condenser at time 0 due to a pulse of magnitude q at time $-t$ is qe^{-lt}.

The expected value of Q is therefore

(26) $$\bar{Q} = \int_0^{T'} qe^{-lt}M\, dt = aq(1 - e^{-lT'})$$

where T' is the interval during which pulses have been arriving before $t = 0$. For large T',

(27) $$\bar{Q} = aq, \quad a = MRC.$$

If q_i, q_j are the contributions due to pulses at times $-t_i, -t_j$,

$$Q^2 = \sum_i q_i^2 + 2\sum_{j<i} q_i q_j.$$

Hence

$$E(Q^2) = Mq^2 \int_0^{T'} e^{-2lt_i} dt_i + 2M^2 q^2 \int_0^{T'} \int_{t_i}^{T'} e^{-lt_i} e^{-lt_j} dt_j dt_i$$

(28) $$= \frac{Mq^2}{2l}(1 - e^{-2lT'}) + \frac{M^2 q^2}{l^2}(1 - e^{-lT'})^2.$$

From (26) and (28)

(29) $$\mathrm{Var}\,(Q) = \tfrac{1}{2} a q^2 (1 - e^{-2lT'})$$

which for large T' is practically $\tfrac{1}{2} a q^2$.

In practice the meter is read either at regular intervals or continuously over a certain period of time and an average value is obtained. The successive readings are not independent, because of the exponential decay. If the readings are taken at times $i\theta/l$, $i = 1, 2, \ldots, n$, and if Q_j, Q_k correspond to values j and k of i, it is easily shown that the coefficient of correlation between Q_j and Q_k is $e^{-(k-j)\theta}$. The variance of $\bar{Q}$ is given by

(30) $$\mathrm{Var}(\bar{Q}) = \frac{aq^2[n(1 - e^{-2\theta}) - 2e^{-\theta}(1 - e^{-n\theta})]}{2n^2 \; (1 - e^{-\theta})^2}$$

as shown by Burgess (Ref. 1). If the observations are taken continuously for a time T_0,

(31) $$\mathrm{Var}(\bar{Q}) = \frac{aq^2}{l^2 T_0^2}(lT_0 - 1 + e^{-lT_0}),$$

which is the limiting form of (30) when $n = lT_0/\theta$ and θ tends to zero.

To find the mean deviation of Q it seems to be necessary to know the probability density for Q. An integral expression can be obtained for this, but evaluation is possible only by approximation.

By methods already indicated, the moments and cumulants of the distribution of Q can be calculated. We find for these cumulants

(32) $$\kappa_1 = aq, \quad \kappa_2 = aq^2/2, \quad \kappa_3 = aq^3/3, \quad \kappa_4 = aq^4/4$$

where $a = MRC$ (often around 6 or 8).

The characteristic function of $f(Q)$ is

$$C(s) = \int_0^\infty e^{iQs} f(Q) dQ = L(-is)$$

where $L(s)$ is the L.T. of $f(Q)$. The cumulant generating function is

$$K(is) = \log L(-is) = \kappa_1(is) + \frac{\kappa_2}{2!}(is)^2 + \ldots$$

$$= a\int_0^{qs}(e^{iu} - 1)du/u$$

(33) $$= a[\mathrm{Ci}(qs) + i\,\mathrm{Si}(qs) - \log qs - \gamma]$$

where the Ci and Si functions are the well-known and fully-tabulated (Ref. 7) integral sine and integral cosine, defined by

$$\mathrm{Ci}(x) = \int_{-\infty}^{x}\frac{\cos u}{u}\,du = \gamma + \log x + \int_0^x\frac{\cos u - 1}{u}\,du,$$

$$\mathrm{Si}(x) = \int_0^x\frac{\sin u}{u}\,du,$$

and γ is Euler's constant, $0.5772\ldots$.

By a well-known inversion theorem on characteristic functions (Ref. 5, p. 91), the probability density $f(Q)$ is given by

$$f(Q) = \frac{1}{2\pi}\int_{-\infty}^{\infty}C(s)\,e^{-iQs}ds$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty}e^{K(-is)}e^{-iQs}ds$$

(34) $$= \frac{1}{\pi}e^{-a\gamma}\int_0^{\infty}(qs)^{-a}e^{a\,\mathrm{Ci}(qs)}\cos\left[Qs - a\,\mathrm{Si}(qs)\right]ds$$

since ($f(Q)$ being obviously real) the integral corresponding to the sine part of the exponential vanishes, and the remaining part of the integrand is an even function of s.

The integrand in (34) is an oscillating function with decreasing amplitude as s increases. Since

(35) $$\begin{cases} \displaystyle\int_0^{qs}(1 - \cos u)\,du/u = T_2 - T_4 + \ldots \\[2mm] \text{and}\quad \displaystyle\int_0^{qs}\sin u\,du/u = T_1 - T_3 + \ldots \end{cases}$$

where $T_k = (qs)^k/(k.k!)$, we have

$$f(Q) = \frac{1}{\pi}\int_0^{\infty}e^{-a(T_2-T_4+\ldots)}\cos(Qs - aT_1 + aT_3 - \ldots)ds.$$

For fairly large values of a the integrand will be appreciable only for small values of s, so that the higher terms in the series in (35) can be neglected. The first approximation, given by neglecting all terms in the series beyond T_2, is

$$f(Q) \approx \frac{1}{\pi}\int_0^{\infty}e^{-aq^2s^2/4}\cos\left[(Q - aq)s\right]ds$$

(36) $$= \frac{1}{q(\pi a)^{\frac{1}{2}}}e^{-(Q-aq)^2/aq^2}$$

which is a normal distribution with mean aq and variance $aq^2/2$. The second approximation, including T_3 and T_4, gives

(37) $\quad f(Q) = \dfrac{1}{q(\pi a)^{\frac{1}{2}}} \, e^{-\theta^2/2} \left[1 + \dfrac{1}{8a} - \left(\dfrac{2}{a}\right)^{\frac{1}{2}} \dfrac{\theta}{3} - \dfrac{1}{4a}\,\theta^2 + \left(\dfrac{2}{a}\right)^{\frac{1}{2}} \dfrac{\theta^3}{9} + \dfrac{1}{24a}\,\theta^4 \right]$

where

$$\theta = (2/a)^{\frac{1}{2}}(Q/q - a).$$

On integration this gives

(38) $\qquad \displaystyle\int_0^\infty f(Q)\,dQ = \Phi(2a)^{\frac{1}{2}} - \left(\dfrac{a}{\pi}\right)^{\frac{1}{2}} e^{-a}\left(\dfrac{1}{12} - \dfrac{1}{8a}\right)$

instead of 1,

where $\qquad\qquad \Phi(x) = (2\pi)^{-\frac{1}{2}} \displaystyle\int_{-\infty}^{x} e^{-\theta^2/2}d\theta.$

For $a = 8$ the right-hand side of (38) is equal to 0.99993. With this value of $f(Q)$ we find $\kappa_1 = aq$, $\kappa_2 = aq^2/2$, and $\kappa_3 = aq^3/3$ approximately. For $a = 8$ the error in κ_3 is about 2%.

The mean deviation can be calculated from the approximation (37) by the relation

(39) $\qquad \delta(Q) = \displaystyle\int_0^E (E - Q)\,f(Q)\,dQ + \int_E^\infty (Q - E)\,f(Q)\,dQ$

where $E = E(Q)$. On evaluating the integrals the result is a long expression which for large a reduces to

(40) $\qquad\qquad \delta(Q) = q\left(\dfrac{a}{\pi}\right)^{\frac{1}{2}} \left(1 - \dfrac{1}{24a}\right).$

A still simpler approximation to the probability density of Q is the Poisson function,

(41) $\qquad\qquad f(Q) = 2q^{-1}p(2a - 1; 2Qq^{-1}).$

It is easily shown that

$$\int_0^\infty f(Q)dQ = 1,$$

and the moments are readily calculated. The quantity $(2a - 1)!$ when $2a$ is not integral is interpreted as $\Gamma(2a)$.

Since (41) is the same function as $f_m(t)$ in (1) with $M = 2q^{-1}$ and $m = 2a$, the first four cumulants are aq, $aq^2/2$, $aq^3/2$, and $3aq^4/4$, instead of the true values, aq, $aq^2/2$, $aq^3/3$, and $aq^4/4$. The mean deviation is, by (3),

(42) $\qquad\qquad \delta(Q) = 2aq\,p(2a; 2a)$

which, by Stirling's approximation, gives

$$\delta(Q) \approx q\left(\dfrac{a}{\pi}\right)^{\frac{1}{2}}\left(1 - \dfrac{1}{24a}\right)$$

in agreement with (40).

For given values of a, q, and Q the exact integral (34) can be evaluated by numerical integration. Some values so calculated are shown in Table I for $q = 1$, $a = 5$. It will be seen that even for so small a value of a the approximation (37) is reasonably good, and considerably better than (41).

TABLE I

PROBABILITY DENSITY OF CHARGE Q

Q	$f(Q)$		
	Quadrature	Approximation (37)	Approximation (41)
1	.002	.004	.000
2	.036	.036	.027
3	.113	.124	.138
4	.239	.232	.248
5	.256	.259	.250
6	.190	.184	.175
7	.104	.096	.095
8	.045	.043	.043
9	.016	.017	.017
10	.005	.005	.006

TABLE II

MEAN DEVIATION

a	Regular	Random	Ratio (r)
50	.250	3.99	16.0
20	.250	2.52	10.1
10	.250	1.78	7.1
5	.250	1.25	5.0

A desirable feature of the mean deviation meter is a high value of the ratio of "random to regular" for the mean deviation. This ratio is given by (25) and (40).

$$(43) \qquad r = \frac{\left(\dfrac{a}{\pi}\right)^{\frac{1}{2}}\left(1 - \dfrac{1}{24a}\right)}{2a^2(e^b - b - 1)}, \quad e^{-b} = a(1 - e^{-1/a}).$$

Some values of δ and r for selected values of a are given in Table II (with $q = 1$). The ratio is independent of q.

7. COMPARISON OF DEVIATION FOR TWO TANKS WITH DIFFERENT DECAY CONSTANTS

In the mean deviation meter (Ref. 4), two tank circuits with different decay constants l_1 and $l_2(l_1 < l_2)$ receive the same system of irregularly spaced pulses, but the heights of the pulses are so adjusted that the average charge is the same for each. The meter measures the integrated absolute difference of the quantities Q_1 and Q_2.

In the calibration of the instrument regularly spaces pulses are used, of period $M^{-1} = T$. By (22), $\bar{Q} = Mq_1/l_1 = Mq_2/l_2$. The average value of $|Q_1 - Q_2|$ is $M \int_0^T |Q_1 - Q_2| dt$. If T' is the value of t for which $Q_1 = Q_2$,

$$(44) \qquad T' = \frac{1}{l_2 - l_1} \log\left(\frac{l_2}{l_1} \cdot \frac{1 - e^{-l_1 T}}{1 - e^{-l_1 T}}\right).$$

In practice $l_1 T$ is of the order 10^{-3} and $l_2 T$ of the order 1, so that $e^{-l_1 T}$ can be written as $1 - l_1 T$ approximately, and

$$T' \approx \frac{1}{l_2 - l_1} \log\left(\frac{l_2 T}{1 - e^{-l_1 T}}\right).$$

Then
$$\overline{|Q_1 - Q_2|} = M\int_0^{T'} (Q_2 - Q_1)dt + M\int_{T'}^{T} (Q_1 - Q_2)dt$$

$$(45) \qquad = \bar{Q}\left[\coth\frac{l_2 T}{2} - \coth\frac{l_1 T}{2} + \frac{l_2 - l_1}{l_1}\frac{2e^{-l_1 T'}}{1 - e^{-l_1 T}}\right].$$

Using the approximation suggested and remembering that l_1/l_2 is very small, we obtain

$$\overline{|Q_1 - Q_2|} \approx \bar{Q}\coth(l_2 T/2)$$

$$(46) \qquad \approx \frac{2\bar{Q}}{l_2 T}\left(1 + \frac{(l_2 T)^2}{12}\right).$$

We now consider the case of random input with a mean counting rate M. If $a_1 = M/l_1$ and $a_2 = M/l_2$, and if $\bar{Q}$ is the same for both tanks,

$$(47) \qquad \begin{cases} \bar{Q} = a_1 q_1 = a_2 q_2, \\ \text{Var}(Q_1) = a_1 q_1^2/2 = \bar{Q}^2/2a_1, \\ \text{Var}(Q_2) = a_2 q_2^2/2 = \bar{Q}^2/2a_2 \end{cases}$$

but Q_1 and Q_2 are not independent since the same succession of pulses is registered in both tanks. A pulse at time $-t$ contributes an amount $q_2 e^{-l_2 t} - q_1 e^{-l_1 t}$ to the total difference $Q_2 - Q_1$ at time 0. The variance of $Q_2 - Q_1$ is

$$\text{Var}(Q_2 - Q_1) = M\int_0^{\infty} (q_2 e^{-l_2 t} - q_1 e^{-l_1 t})^2 dt$$

$$+ 2M^2\int_0^{\infty}\int_t^{\infty} (q_2 e^{-l_2 t} - q_1 e^{-l_1 t})(q_2 e^{-l_2 t'} - q_1 e^{-l_1 t'})dt' \, dt$$

$$(48) \qquad = \bar{Q}^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{2}{a_1 + a_2}\right)$$

$$\approx \bar{Q}^2/2a_2.$$

From (47) and (48)

$$(49) \qquad \text{Cov}(Q_1, Q_2) = \bar{Q}^2(a_1 + a_2)^{-1}.$$

Successive cumulants of the distribution of $Q_2 - Q_1$ may be calculated in a similar way. Thus

$$(50) \qquad \kappa_3 = \frac{2}{3} \bar{Q}^3 \frac{(a_1 - a_2)^3 (a_1 + a_2)}{a_1^2 a_2^2 (a_1 + 2a_2)(2a_1 + a_2)},$$

$$(51) \qquad \kappa_4 = \frac{3}{4} \bar{Q}^4 \frac{(a_1 - a_2)^4 (a_1^2 + 3a_1 a_2 + a_2^2)}{a_1^3 a_2^3 (a_1 + 3a_2)(3a_1 + a_2)(a_1 + a_2)}.$$

If we neglect powers of a_2/a_1 higher than the first, we get

$$\kappa_1 = 0, \quad \kappa_2 = \frac{\bar{Q}^2}{2a_2}\left(1 - \frac{3a_2}{a_1}\right) = \frac{a_2 q_2^2}{2} - \frac{3}{2}\frac{a_2^2}{a_1}q_2^2,$$

$$\kappa_j = \frac{\bar{Q}^j}{ja_2^{j-1}}\left(1 - \frac{j^2 a_2}{(j-1)a_1}\right) = \frac{a_2 q_2^j}{j} - \frac{j}{j-1}\frac{a_2^2}{a_1}q_2^j, \quad j > 2.$$

The cumulant generating function is

$$K(is) = \sum_{j=1}^{\infty} \kappa_j (is)^j / j!$$

$$(52) \qquad = \left(a_2 - \frac{a_2^2}{a_1}iq_2 s\right)\int_0^{q_2 s} \frac{e^{iu} - 1}{u}\, du - ia_2 q_2 s - \frac{1}{4}\frac{a_2^2}{a_1}(q_2 s)^2.$$

As in Section 6, the probability density function for $x = Q_2 - Q_1$ is

$$(53) \qquad f(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ixs} e^{K(-is)} ds.$$

By similar methods to those in Section 6, we find

$$f(x) = \frac{1}{\pi} e^{-\gamma a_1} \int_0^{\infty} (q_2 s)^{-a_2} \exp\left[a_2 \,\mathrm{Ci}(q_2 s) + \frac{a_2^2 q_2 s}{a_1}\,\mathrm{Si}(q_2 s) - \frac{a_2^2 q_2^2 s^2}{4a_1}\right]$$

$$(54) \quad \times \cos\left[(x + a_2 q_2)s + a_2 \,\mathrm{Si}(q_2 s) - \frac{a_2^2 q_2 s}{a_1}(\gamma + \log(q_2 s) - \mathrm{Ci}(q_2 s))\right] ds$$

$$= \frac{1}{\pi}\int_0^{\infty} \exp\left[a_2(-T_2 + T_4 - \ldots) + \frac{a_2^2}{a_1}T_1(\tfrac{3}{4}T_1 - T_3 + \ldots)\right]$$

$$\times \cos\left[xs + a_2(T_3 - T_5 + \ldots) - \frac{a_2^2}{a_1}T_1(T_2 - T_4 + \ldots)\right] ds$$

where $T_j = (q_2 s)^j / j.j!$.

A first approximation, including only T_1 and T_2, gives a normal distribution with mean 0 and variance $\frac{1}{2}a_2 q_2^2(1 - 3a_2/a_1)$. The mean deviation, to this approximation, is

$$\delta = q_2(a_2/\pi)^{\frac{1}{2}}(1 - 3a_2/2a_1).$$

The second approximation, including terms in s^4, gives

$$\delta = q_2(a_2/\pi)^{\frac{1}{2}}\left[1 - \frac{1}{24a_2} - \frac{3a_2}{2a_1}\left(1 + \frac{1}{72a_2}\right)\right].$$

By analogy with the results in Section 6, we may look for a solution of the Poisson type,

$$f(x) = 0, \quad x < -b,$$

$$f(x) = k\, p(kx + kb; 2a - 1), \quad x > -b.$$

Choosing k and b so that

$$\kappa_1 = 0, \quad \kappa_2 = \frac{a_2 q_2^2}{2}\left(1 - \frac{3a_2}{a_1}\right)$$

we find

$$b = a_2 q_2\left(1 - \frac{3a_2}{a_1}\right)^{\frac{1}{2}}, \text{ and } k = \frac{2}{q_2}\left(1 - \frac{3a_2}{a_1}\right)^{-\frac{1}{2}}.$$

The value of κ_3 is then $\frac{1}{2} a_2 q_2^3 (1 - 9a_2/a_1)$ and the mean deviation is

$$(55) \qquad \delta(x) = q_2\left(\frac{a_2}{\pi}\right)^{\frac{1}{2}}\left(1 - \frac{3a_2}{2a_1}\right)\left(1 - \frac{1}{24a_2}\right).$$

If $\lambda = a_2/a_1$ (a small fraction),

$$(56) \qquad \frac{\delta(x)}{\bar{Q}} = (\pi a_2)^{-\frac{1}{2}}\left(1 - \frac{1}{24a_2}\right)\left(1 - \frac{3\lambda}{2}\right).$$

When $\lambda \to 0$ we get equation (40) with a_2 instead of a.

REFERENCES

1. BURGESS, R. E. Rev. Sci. Instruments, 20:964. 1949.
2. CLARK, C. E. Rev. Sci. Instruments, 20:51. 1949.
3. FELLER, W. Courant anniversary volume. Interscience Publishers, New York, N.Y. 1948. p. 105.
4. GREENBERG, L. H. and HAPP, W. W. Can. J. Phys. 30:317. 1952. (Fuller details in Greenberg, L. H. Thesis at University of Alberta, Edmonton, Alta. 1950.)
5. KENDALL, M. G. Advanced theory of statistics, Vol. I. Charles Griffin & Co., Ltd., London. 1947.
6. MOLINA, E. C. Poisson's exponential binomial limit. D. Van Nostrand Co., Inc., New York. 1947.
7. National Bureau of Standards, Washington, D.C. Tables of sine, cosine and exponential integrals, Vols. I, II. Tables of sine and cosine integrals for arguments from 10 to 100. New York.
8. PEARSON, K. Table of incomplete gamma function. H. M. Stationery Office, London. 1922.
9. SCHIFF. L. I. and EVANS, R. D. Rev. Sci. Instruments, 7:456. 1936.

NOTE

A Note On The Sensitivity Of Electrical Bridge Networks*

Although at present the absolute resistance of no standard resistor can be pre-sumed to be known to an accuracy much in excess of 0.001%, nevertheless the main standardizing laboratories must be able to compare standard resistors with a relative precision of 0.0001%, or one part in one million (1 p.p.m.). In fact, for the special case of 1-ohm standards now available, a precision of 1 or 2 parts in 10 million is desirable in order to assess the relative changes that may occur in a few months or a year. Also, in order to maintain a scale of resistance, comparisons with a precision of 1 p.p.m. or better are required in order that the end points of the scale, say 0.0001 ohms or 10,000 ohms, may be known with a precision approaching 0.001% or 10 p.p.m.

It is the purpose of this note to present an analytical solution to the problem of determining a scale reading when the bridges are very nearly, but not quite, balanced, which reading corresponds to the true null position, and of assessing the precision of such a determination. This treatment includes the effects of inter-actions from subsidiary bridges used either to eliminate or to evaluate certain correction terms. Previously this problem has been treated in an experimental manner, as may be seen from earlier publications on the subject, such as those by Drysdale (1) and Smith (5), Harris (2) and Wenner (7), Jaeger (3) or Stein-wehr (6), and Romanowski (4), representing various standardizing laboratories. The paper by Wenner (7) contains an excellent bibliography covering all phases of the work.

The most general form of the equation relating the galvanometer current i to the bridge current I is

$$(1) \qquad i = f(I, X, a, b, \ldots, \alpha, \beta, \gamma)$$

where X is the resistance to be measured, $a, b, \ldots$ are the fixed resistors of the bridge, and α, β, γ are the variable parameters whose values at true bridge balance will be designated by α^0, β^0, γ^0. The bridge is balanced when the current through the galvanometer produces a deflection of the spot smaller than the minimum perceptible with the equipment.

For practical reasons it is difficult to determine precisely all variables involved and thus it is useful to form other bridges leading to supplementary equations by appropriate changes of connections. By this means it is possible to eliminate all but one of the variable parameters in the final equation which determines the value of the unknown X. Consider the case of three bridges derived from the same network, the simultaneous balances of which can be obtained by a series of suc-cessive approximations. Before the balances are obtained, the equations have the form

$$i_f = f(I_f, X, a, b, \ldots, \alpha, \beta, \gamma),$$

$$(2) \qquad i_g = g(I_g, X, a, b, \ldots, \alpha, \beta, \gamma),$$

$$i_h = h(I_h, X, a, b, \ldots, \alpha, \beta, \gamma).$$

After the balancing, i.e. if $i_f = i_g = i_h = 0$ and $\alpha = \alpha^0$, $\beta = \beta^0$, $\gamma = \gamma^0$, the equations may be solved and presented in the form

$$(3) \qquad X = \lambda(\alpha^0) = \mu(\beta^0) = \nu(\gamma^0).$$

The equation used for the calculation is the one which contains the best known parameter, say α.

If the bridges are not quite balanced, and the parameters have values slightly different from α^0, β^0, γ^0, then let

$$(4) \qquad \alpha = \alpha^0 + \Delta\alpha, \beta = \beta^0 + \Delta\beta, \gamma = \gamma^0 + \Delta\gamma.$$

In this case, equations (3) become of the type

$$(5) \qquad X = \lambda(\alpha - \Delta\alpha) = \lambda(\alpha) - \frac{\partial\lambda}{\partial\alpha}\Delta\alpha.$$

The effect of the quantities $\Delta\alpha$, $\Delta\beta$, $\Delta\gamma$ is to produce deflections of the galvanometer, $\Delta\theta_f$, $\Delta\theta_g$, $\Delta\theta_h$. If $\Delta\alpha$, $\Delta\beta$, $\Delta\gamma$ are considered as very small quantities producing only small currents Δi_f, Δi_g, Δi_h, then total differentiation of (2) establishes relations of the type

$$(6) \qquad \frac{\partial f}{\partial\alpha}\Delta\alpha + \frac{\partial f}{\partial\beta}\Delta\beta + \frac{\partial f}{\partial\gamma}\Delta\gamma = \Delta i = \sigma\Delta\theta_f$$

where $\sigma = \dfrac{\Delta i_f}{\Delta\theta_f} = \dfrac{\Delta i_g}{\Delta\theta_g} = \dfrac{\Delta i_h}{\Delta\theta_h} =$ sensitivity of the galvanometer. By solving equations (6) for $\Delta\alpha$ and introducing the value found into the first of the equations (5) one obtains a value of X in terms of α and a "secondary" term containing the deflections $\Delta\theta_f$, $\Delta\theta_g$, $\Delta\theta_h$, and the bridge currents I_f, I_g, I_h. If the smallest perceptible deflections of the galvanometer are represented by $\pm\,\delta\theta_f$, $\pm\,\delta\theta_g$, $\pm\,\delta\theta_h$, then the secondary term gives the upper limit of the "sensitivity error".

Application of this method to the well-known Wheatstone Bridge (Fig. 1) for which equation (1) becomes

$$(7) \qquad i = I\frac{AS - BX}{G(A + B + X + S) + (A + X)(B + S)}$$

gives the standard relation

$$(8) \qquad X = \frac{A}{B}S - \left(\frac{G(A + B + X + S) + (A + X)(B + S)}{B}\right)\frac{\sigma}{I}\Delta\theta.$$

For this case of only one variable, it is not necessary to calculate the coefficient of $\Delta\theta$ in the secondary term as it may be obtained experimentally by interpolation of galvanometer deflections.
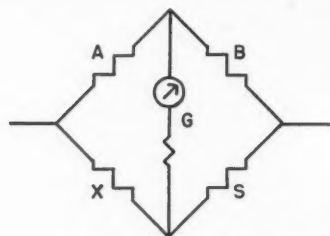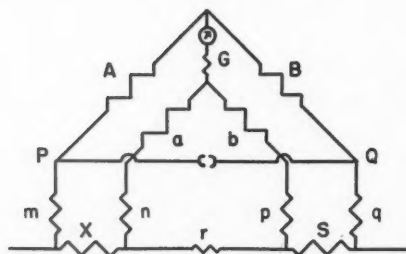
FIG. 1. Wheatstone Bridge.

FIG. 2. Kelvin Double Bridge.

For a Kelvin Double Bridge (Fig. 2) the general equations are long, but the equations for a balanced bridge are relatively simple. Of the many bridges it is possible to form from the basic network, for three often constructed the balance equations are as follows:

(a) Main Double Bridge: variable $A (\equiv a)$

$$(9) \qquad \frac{X}{S} - \frac{A^0 + m^0}{B + q} + \frac{b + p}{S} \frac{r}{a + b + r + n + p} \left(\frac{a^0 + n}{b + p} - \frac{A^0 + m^0}{B + q} \right) = 0.$$

(b) Second Double Bridge: short circuit between P and Q (thus $A = B = 0$); variable $m(\equiv \beta)$

$$(10) \qquad \frac{X}{S} - \frac{m^0}{q} + \frac{b + p}{S} \frac{r}{a + b + r + n + p} \left(\frac{a^0 + n}{b + p} - \frac{m^0}{q} \right) = 0.$$

(c) Wheatstone Bridge: connection PQ and link r open; variable $a(\equiv \gamma)$

$$(11) \qquad \frac{a^0 + n + X}{b + p + S} - \frac{A^0 + m^0}{B + q} = 0.$$

These three equations may be solved for any of the variables A, a, or m. It will be assumed that A is the best known, and consequently the solution

$$(12) \qquad X = \frac{A^0}{B} S$$

will be considered. If the bridges are not all balanced, then if $A = A^0 + \Delta A$, the solution becomes

$$(13) \qquad X = \frac{A}{B} S - \frac{\Delta A}{B} S.$$

Solution of the equations (6) to give ΔA in terms of $\Delta\theta_f$, $\Delta\theta_g$, $\Delta\theta_h$ leads to a lengthy relation* for the secondary term. A simplified form, suitable for numerical calculations (assuming $1 - \dfrac{r}{a+b} \equiv 1$ and $1 + \dfrac{q}{B} \equiv 1$) is:

$$(14) \qquad \frac{\Delta A}{B} S = \frac{\sigma}{B}\left[\frac{\Sigma_f}{I_f}\Delta\theta_f - \frac{\Sigma_g}{I_g}\left(1 + \frac{b}{S}\frac{r}{a+b}\right)^{-1}\Delta\theta_g - \frac{\Sigma_h}{I_h}\frac{r}{a+b}\Delta\theta_h\right]$$

where

$$(15) \qquad \Sigma_f = \left(G + \frac{ab}{a+b}\right)(A + B + X + S + m + q)$$

$$+ (A + X + m)(B + S + q),$$

$$(16) \qquad \Sigma_g = \left(G + \frac{ab}{a+b} + \frac{AB}{A+B}\right)(X + S + m + q)$$

$$+ (X + m)(S + q),$$

$$(17) \qquad \Sigma_h = G(A + B + a + b + X + S + m + n + p + q)$$

$$+ (A + a + X + m + n)(B + b + S + p + q).$$

The Kelvin Double Bridge† used for intercomparison of precision standard resistors in this laboratory is essentially the same as the one described in Wenner's paper (1, pp. 244-258). As an example of this method, Table I shows the sensitivity errors expected when comparing nominally equal standards in the range from 10 ohms to 0.0001 ohms. The constants of the bridge used in formulae (14)-(17) are as follows:

$$A = B = 2a = 2b = 25 \text{ ohms}, \quad r = 0.05 \text{ ohm},$$

$$m = q = 1 \text{ ohm}, \qquad\qquad n = p = 0.01 \text{ ohm},$$

$$G = 70 \text{ ohms} \ (60 \text{ ohms for } 10 \text{ ohm comparison}).$$

$$* \frac{\Delta A}{B} S = \frac{\sigma \Delta\theta_f \Sigma_f}{I_f}\left(\frac{1}{(B+q)\left(1 - \dfrac{r}{a+b}\right)} + \frac{q}{B(B+q)\left(1 + \dfrac{b}{S}\dfrac{r}{a+b}\right)}\right)$$

$$- \frac{\sigma\Delta\theta_g\Sigma_g}{I_g}\left(\frac{1}{B\left(1 + \dfrac{b}{S}\dfrac{r}{a+b}\right)}\right) - \frac{\sigma\Delta\theta_h\Sigma_h}{I_h}\left(\frac{\dfrac{r}{a+b}}{(B+q)\left(1 - \dfrac{r}{a+b}\right)}\right)$$

† *Constructed by Eppley Laboratories Inc., Newport, R. I.*

TABLE I

Typical sensitivity errors for various resistance comparisons

$X = S$ (ohm)	$I_f = I_g$ (amp.)	I_h (amp.)	Sensitivity error due to			Net sensitivity error
			1st Bal. (ohm)	2nd Bal. (ohm)	3rd Bal. (ohm)	$\frac{\Delta A}{B} S$
10	0.060	0.015	1.46×10^{-6}	0.46×10^{-6}	0.02×10^{-6}	1.94×10^{-6} ohm $= 0.20$ p.p.m.
1	0.150	0.020	5.16×10^{-7}	0.38×10^{-7}	0.12×10^{-7}	5.66×10^{-7} ohm $= 0.57$ p.p.m.
0.1	0.500	0.020	14.90×10^{-8}	0.52×10^{-8}	1.10×10^{-8}	16.52×10^{-8} ohm $= 1.65$ p.p.m.
0.01	3.5	0.030	21.24×10^{-9}	0.24×10^{-9}	7.36×10^{-9}	28.82×10^{-9} ohm $= 2.88$ p.p.m.
0.001	7.5	0.075	99.2×10^{-10}	1.6×10^{-10}	28.8×10^{-10}	129.6×10^{-10} ohm $= 13.0$ p.p.m.
0.0001	25	0.100	296×10^{-11}	1.6×10^{-11}	216×10^{-11}	514×10^{-11} ohm $= 51.4$ p.p.m.

The galvanometer sensitivity is 4×10^{-10} amp. per mm. at a scale distance of 1300 mm. (i.e. $\sigma = 4 \times 10^{-10} \times 1300 = 5.2 \times 10^{-7}$ amp.). It is assumed that galvanometer deflections of up to one millimeter are tolerated rather than having true null indication for each balance $\left(\text{i.e. } \Delta\theta_f = \Delta\theta_g = \Delta\theta_h = \pm \dfrac{1\text{mm.}}{1300 \text{ mm.}} \right)$.

The figures in Table I immediately show the relative importance of each of the three balances in the net precision of any high quality intercomparison. Interpolation to within ± 0.2 mm. rather than ± 1.0 mm. for the first balance ($\Delta\theta_f = \pm 0.2/1300$) will materially improve the expected precision. Also, from formula (14) it is seen that reduction of the value of r from 0.05 ohm to 0.005 ohm will improve the effect of the third balance, particularly for the lower resistance comparisons, although the improvement will be partially lost because of the effect of r on the second balance. As an example, for 0.0001 ohm comparisons with $r = 0.005$ ohm, the expected sensitivity becomes

$$\frac{\Delta A}{B} S = (296 + 16 + 22) \times 10^{-11} = 334 \times 10^{-11} = 33.4 \text{ p.p.m.,}$$

rather than 51.4 p.p.m. in Table I.

The results in Table I are borne out by experience with the bridge in use, the value of r being $0.03 - 0.05$ ohm. Similar results are obtained for the 10:1 ratio comparisons used in obtaining the scale of resistance from the basic 1-ohm standards. In this way the measurement precision of any standard resistor may be readily determined, in so far as the bridge sensitivity is concerned. Other factors, of course, will also affect the final accuracy of measurement.

This treatment has proved of value by indicating the necessary care required in any particular high quality resistor measurement, and has permitted considerable reduction in the time required for making observations by showing those places in which relatively large galvanometer deflections may be tolerated at the "null-point" or where extra care in balancing is required. The treatment may be useful to others interested in obtaining the utmost precision and flexibility from similar pieces of equipment.

1. DRYSDALE, C. V. Electrician, 60: 20; 53. 1908.
2. HARRIS, F. K. Electrical measurements. John Wiley and Sons, Inc., New York. 1952. Chap. 7.
3. JAEGER, W. Z. Instrumentenk. 26: 69; 73; 360. 1906.
4. ROMANOWSKI, M. Rev. gén. élec. 48: 41. 1940.
5. SMITH, F. E. Electrician, 57: 976, 1009. 1906; 60: 471, 566. 1908.
6. STEINWEHR, H. V. *In* Handbuch der Physik. Vol. XVI. Verlag von Julius Springer, Berlin. 1927. Chap. 17.
7. WENNER, F. J. Research Natl. Bur. Standards, 25: 229. 1940.

M. ROMANOWSKI
A. F. DUNN
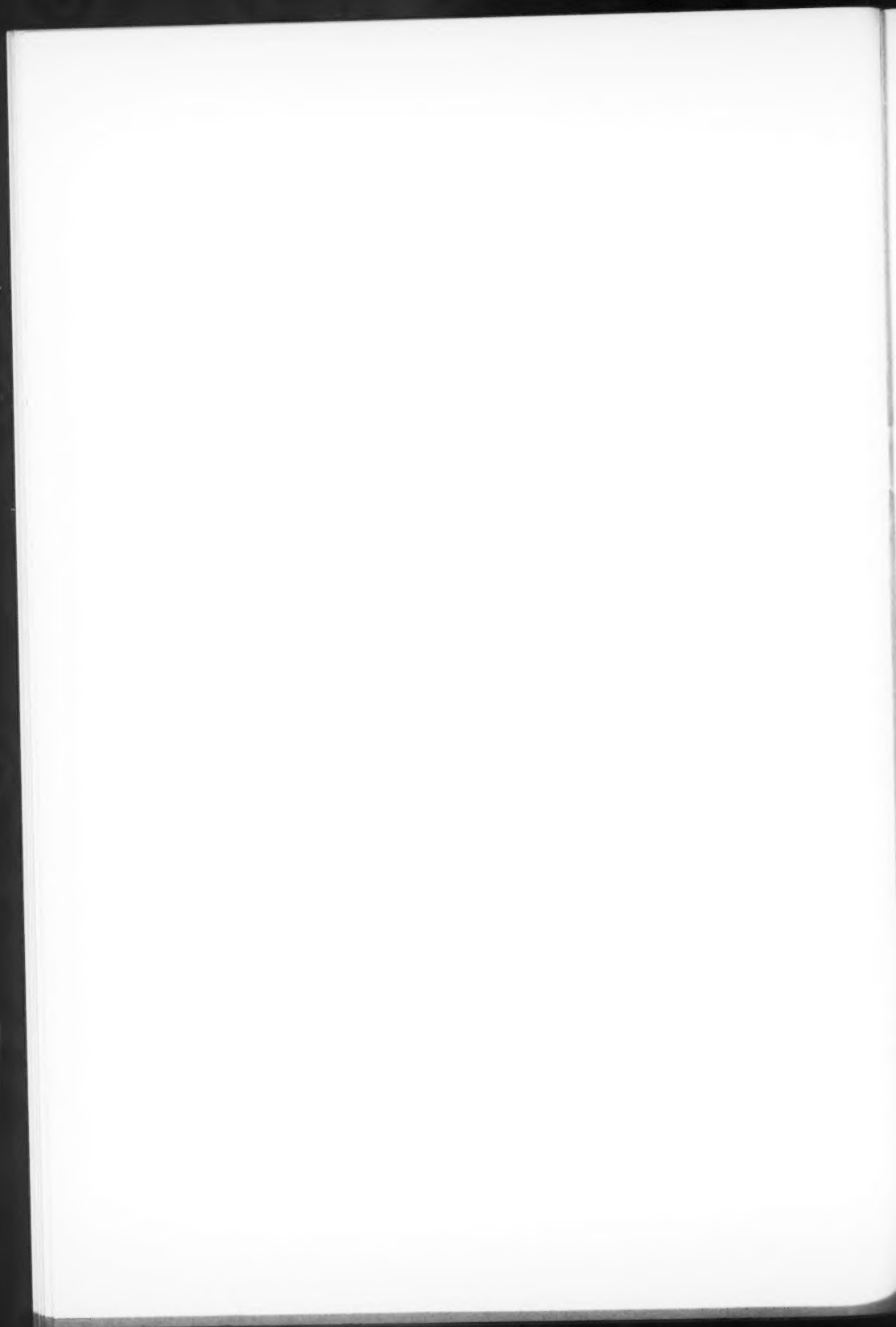
GENERAL: Manuscripts should be typewritten, double spaced, and the **original and one extra copy** submitted. Style, arrangement, spelling, and abbreviations should conform to the usage of this Journal. Names of all simple compounds, rather than their formulas, should be used in the text. Greek letters or unusual signs should be written plainly or explained by marginal notes. Superscripts and subscripts must be legible and carefully placed. Manuscripts should be carefully checked before being submitted, to reduce the need for changes after the type has been set. If authors require changes to be made after the type is set, they will be charged for changes that are considered to be excessive. **All pages, whether text, figures, or tables, should be numbered.**

ABSTRACT: **An abstract of not more than about 200 words, indicating the scope of the work and the principal findings, is required.**

ILLUSTRATIONS:

(i) *Line Drawings:* All lines should be of sufficient thickness to reproduce well. Drawings should be carefully made with India ink on white drawing paper, blue tracing linen, or co-ordinate paper **ruled in blue only;** any co-ordinate lines that are to appear in the reproduction should be ruled in black ink. Paper ruled in **green, yellow, or red should not be used** unless it is desired to have all the co-ordinate lines show. Lettering and numerals should be neatly done in India ink preferably with a stencil (**do not use typewriting**) and be of such size that they will be legible and not less than one millimeter in height when reproduced in a cut three inches wide. All experimental points should be carefully drawn with instruments. Illustrations need not be more than two or three times the size of the desired reproduction, but the ratio of height to width should conform with that of the type page. **The original drawings and one set of small but clear photographic copies are to be submitted.**

(ii) *Photographs:* Prints should be made on glossy paper, with strong contrasts; they should be trimmed to remove all extraneous material so that essential features only are shown. Photographs should be submitted **in duplicate;** if they are to be reproduced in groups, one set should be so arranged and mounted on cardboard with rubber cement; the duplicate set should be unmounted.

(iii) *General:* **The author's name, title of paper, and figure number should be written in the lower left hand corner (outside the illustration proper) of the sheets on which the illustrations appear.** Captions should not be written on the illustrations, but typed together at the end of the manuscript. All figures (including each figure of the plates) should be numbered consecutively from 1 up (arabic numerals). **Each figure should be referred to in the text.** If authors desire to alter a cut, they will be charged for the new cut.

TABLES: Each table should be typed on a separate sheet. Titles should be given for all tables, which should be numbered in Roman numerals. Column heads should be brief and textual matter in tables confined to a minimum. **Each table should be referred to in the text.**

REFERENCES: **These should be listed alphabetically by authors' names, numbered in that order, and placed at the end of the paper.** The form of literature citation should be that used in this Journal. **Titles of papers should not be given.** The first page only of the references cited should be given. **All citations should be checked with the original articles.** Each citation should be referred to in the text by means of the key number.

REPRINTS: A total of 50 reprints of each paper, without covers, are supplied free to the authors. Additional reprints will be supplied according to a prescribed schedule of charges. On request, covers can be supplied at cost.

Approximate charges for reprints may be calculated from the number of printed pages, obtained by multiplying by 0.6 the number of manuscript pages (double-spaced typewritten sheets, $8\frac{1}{2}$ in. by 11 in.) and making allowance for space occupied by line drawings and half-tones (not inserts). The cost per page is tabulated at the back of the reprint request form sent with the galley.

Contents